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THE CATALYSIS OF THERMAL DECOMPOSITION AND
BURNING REACTIONS OF FUEL-OXIDANT COMPOSITIONS

Final Report

by

E. S. Freeman and W. Rudloff
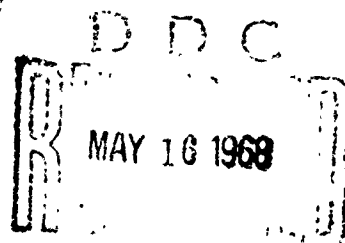
May 1968

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Chemical Research Laboratory
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# THE CATALYSIS OF THERMAL DECOMPOSITION AND BURNING REACTIONS OF FUEL-OXIDANT COMPOSITIONS

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Eli S. Freeman and Winfried K. Rudloff

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## FOREWORD

The work described in this report was authorized under Project 1C014501B71A, Life Sciences Basic Research in Support of Materials, Chemical (U). This work was started on October 3, 1966 and completed September 30, 1967.

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## ACKNOWLEDGMENTS

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## DIGEST

The effects of defect structure and of doping potassium chlorate on its chemical reactivity with respect to its self-propagative reactions with sulfur were investigated.
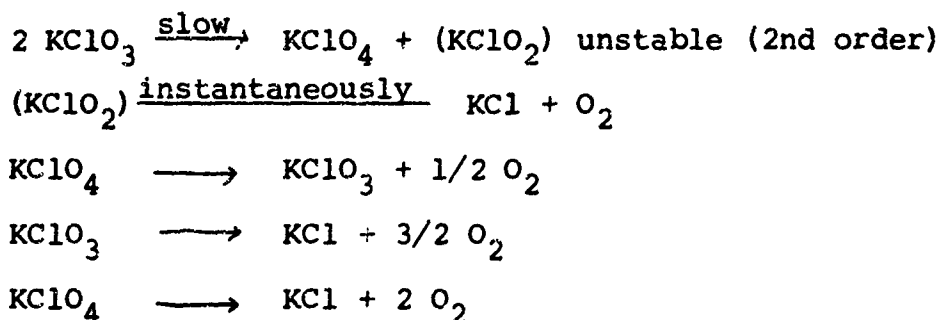
The preparations of doped single crystals of potassium chlorate continued throughout the entire program. Selected single crystals were analyzed for their dopant contents. The influence of doping, irradiation and mechanical shock on the thermal decomposition of potassium chlorate was investigated by differential thermal analysis (DTA) and thermogravimetric analysis, (TGA). Intimate mixtures of sulfur and doped potassium chlorates were also investigated with respect to their combustion properties by means of DTA and TGA.

The effects of potassium perchlorate and potassium chloride as an intermediate reaction product on the thermal decomposition of potassium chlorate were studied. These experiments were necessary for establishing the basis for evaluating the reactivity of $KClO_3$ with sulfur.

Electrical conductivity studies were conducted to correlate electronic defect structure with the reactivity behavior of $KClO_3$. Low temperature isothermal investigations were conducted to evaluate possible reaction mechanisms.

The results of the investigations are summarized as follows:

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1. The results indicate that the decomposition of potassium chlorate occurs in the following steps:

$$2 \; KClO_3 \xrightarrow{\text{slow}} KClO_4 + (KClO_2) \; \text{unstable (2nd order)}$$

$$(KClO_2) \xrightarrow{\text{instantaneously}} KCl + O_2$$

$$KClO_4 \longrightarrow KClO_3 + 1/2 \; O_2$$

$$KClO_3 \longrightarrow KCl + 3/2 \; O_2$$

$$KClO_4 \longrightarrow KCl + 2 \; O_2$$

The first disproportionation reaction is consistent with a second order mechanism. This reaction is inhibited at low temperatures by excessive amounts of KCl. At higher temperatures, KCl catalyzes the reaction.

$KClO_4$ does not catalyze decomposition of $KClO_3$. At higher concentrations, the decomposition of $KClO_3$ is inhibited in the presence of $KClO_4$.

2. The order of dopants with respect to decreasing the decomposition temperatures of doped $KClO_3$ was found to be: the most effective, $FeCl_3 > CuCl_2 > Pb(NO_3)_2 > CdCl_2 > LiNO_3 > LiCl \sim KCl \sim CsCl \sim$ No Dopant. This order may be correlated to charge density or to charge transfer. Doping $KClO_3$ with nitrates reduces the temperature of the DTA endotherm for melting.

3. Gamma irradiation and mechanical shock influences the decomposition path of $KClO_3$. Low temperature weight loss and smell of chlorine and/or chlorine oxides point to defect creation of possible radicals such as $ClO_3$ within the crystalline lattice due to irradiation. An exotherm appears at about 75°C in the DTA curve for the mechanically shocked sample which does not appear in the untreated sample.

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4.    Doping of $KClO_3$ significantly influences the ignition of mixtures of $KClO_3$ and sulfur. Two effects are apparent: The order of ignition temperatures with reference to the dopants is: lowest for $CuCl_2 \ll KCl \sim$ undoped $\sim CsCl \sim Pb(NO_3)_2 < FeCl_3 \lesssim CdCl_2 < LiCl \sim LiNO_3 \sim CaCl_2$.

The extent of total weight loss as measured in the TGA experiment is dependent on the rate of combustion since the rapid ignition forces material out of the reaction vessel. This appears to be true particularly for the $FeCl_3$ doped samples. $Fe^{+++}$ and $Cu^{++}$ doped $KClO_3$ appears to react slowly at room temperature with sulfur.

5.    The reactivity of sulfur-$KClO_3$ mixtures is especially affected by the presence of $Fe_2O_3$ catalyst. In oxygen the ignition temperature of the sulfur-potassium chlorate mixture is significantly lowered in the presence of the $Cr_2O_3$ and $Fe_2O_3$ catalysts.

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## THE CATALYSIS OF THERMAL DECOMPOSITION AND
## BURNING REACTIONS OF FUEL-OXIDANT COMPOSITIONS

### I.   INTRODUCTION

In a previous study sponsored by Edgewood Arsenal, Contract No. DA-18-035-AMC-341(A), "Mechanistic Investigation of Catalysis of Thermal Decomposition Reactions" the importance of defect structure in relationship to the heterogeneous catalytic decomposition of potassium chlorate was investigated. This research was extended in the present program to consider the catalytic effects resulting from the presence of small quantities of foreign ions crystallized out of solution with potassium chlorate and to consider the effects of defect structure introduced by doping and various physical treatments. It was shown in previous studies conducted by Dr. Eli S. Freeman[1,2] that doping with cationic and anionic impurities and exposure to high energy radiation profoundly altered the chemical reactivity of oxidants and fuel such as ammonium perchlorate, potassium perchlorate, and magnesium powder. Another interesting effect in the case of the potassium perchlorate-magnesium mixture is that reproducibility with respect to time to ignition was improved by doping.

The objective of this program was to investigate the relationships between the defect structure of potassium chlorate and its chemical reactivity with respect to thermal decomposition and its reaction with sulfur. The long range goal is to provide information which would establish the basis for the improvement of pyrotechnic compositions.

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In this present program two methods of doping were used
The first was evaporation of solutions to dryness and the other
principal method was crystallization from aqueous solutions.
The crystallization procedures involved the collection of crops
of crystals as a function of time in solutions of varying con-
centrations. Spectroscopic procedures were used to analyze for
the dopant ion concentrations.

Some of these doping ions will form oxides and chloride
phases during decomposition which may serve as nuclei for de-
composition. Another result of crystallizing potassium chlorate
in the presence of small quantities of impurity ions will be the
formation of defect structure in the potassium chlorate crystal.
It was of interest to investigate the effect that crystal de-
fects including lattice vacancies, dislocations and strains can
have in catalyzing the decomposition of potassium chlorate.
Another interesting aspect of the research was to investigate
the possible electron transfer processes on the surfaces of the
crystal and molten oxidant and fuel such as sulfur. The catalytic
effects resulting from exposure to high energy radiation, such
as gamma rays on the propagative reactions between oxidants and
fuels as well as defects introduced by mechanical shock was
also included in this program.

The experimental methods for investigating the decomposition
rates of the oxidants, the oxidation of the fuels and pre-igni-
tion reactions of the oxidant-fuel mixtures were principally
thermogravimetry and differential thermal analysis and electrical
conductivity measurements.

## II. EXPERIMENTAL

### A. Preparation and Standardization of Samples

#### 1. Preparation and Standardization of Heterocrystalline Doped Samples of Potassium Chlorate

The following doped chlorates were prepared by evaporating solutions of $KClO_3$ containing 1 mole percent of the dopants to dryness on a hot water bath:

(a) $KClO_3$ - 1 mole % LiCl

(b) $KClO_3$ - 1 mole % KCl

(c) $KClO_3$ - 1 mole % CsCl

(d) $KClO_3$ - 1 mole % $CaCl_2$

(e) $KClO_3$ - 1 mole % $CdCl_2$

(f) $KClO_3$ - 1 mole % $CuCl_2$

(g) $KClO_3$ - 1 mole % $FeCl_3$

(h) $KClO_3$ - 1 mole % $LiNO_3$

(i) $KClO_3$ - 1 mole % $PbNO_3$

The crystallized samples were crushed gently in a mortar, sieved, and sieve fractions between 240 and 270 mesh sieves, US standard stainless steel sieves, and stored in a desiccator for further use.

#### 2. Preparation of Doped Single Crystals of Potassium Chlorate by Slow Crystallization Procedures

Preliminary crystallization procedures were done as follows: Various reagent grade chlorates obtained from K & K Laboratories were put in solution with $KClO_3$ in varying concentrations. The concentrations of doping impurities were 0.1, 1, and 10 mole percent. These solutions were then transferred

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into large dishes and subjected to slow crystallization at room temperature as well as at lower temperatures.

Saturated solutions of $KClO_3$ at room temperature were prepared with 0.1, 1 and 10 mole % of the following dopants: $NaClO_3$, $Ba(ClO_3)_2$, $AgClO_3$, $Ca(ClO_3)_2$, and $Cu(ClO_3)_2$.

Crystallization took place slowly over several weeks and resulted in large single crystals. These single crystals were separated from solution, washed with water, and dried and stored in a desiccator for further use.

Further crystallization procedures were developed which involved slow crystallization from doped solutions in large beakers, and crop collection at different stages of crystallization.

Initial crops were collected, dried in a desiccator and submitted for analysis. These crystallizations were in progress until the end of the program. The following dopants were used:

       a.  $NaClO_3$

       b.  $Ba(ClO_3)_2H_2O$

       c.  $Ca(ClO_3)_2 \cdot 2H_2O$

       d.  $AgClO_3$

       e.  $Cu(ClO_3)_2$

### 3. Gamma Irradiation and Shock Treatment of Reagent Grade Potassium Chlorates

Portions of 240-270 mesh $KClO_3$ (reagent grade) were subjected to $Co^{60}$ gamma irradiation of varying doses. The irradiation cell has been described previously.[3] Portions of the irradiated samples were dried in a desiccator at room temperature, and also in an oven at 110°C. Portions were also used for DTA/TGA experiments directly after they were taken from the hot cell.

Some $KClO_3$ was subjected to mechanical shock by pounding and vigorous crushing in a mortar.

### 4. Preparation of Pellets

Pellets of $KClO_3$ were pressed with the hydraulic press under 20,000 psi pressure. These were eventually used in our conductivity experiments.

### 5. Preparation of Mixtures

In order to investigate the influence of doping and of various oxides on the combustion of $KClO_3$ with sulfur, mixtures were prepared of different compositions.

Doped $KClO_3$ was mixed with sulfur corresponding to the stoichiometry of the overall reaction:

$$2KClO_3 + 3S \rightarrow 3SO_2 + 2KCl$$

some mixtures were prepared with excessive $KClO_3$.

The $KClO_3$ in all mixtures was sieved to screen fraction 240 270 for standardization and then stored in a desiccator.

Tertiary mixtures of various mole ratios were also prepared from reagent grade $KClO_3$ with several oxides and with

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sulfur. The sieve-fractions of $KClO_3$ and the oxides between 240 and 270 mesh were used. These mixtures were also stored in a desiccator.

## B. Differential Thermal Analysis, Thermogravimetric Analysis and Isothermal Experiments

DTA and TGA experiments were done on a combined DTA/TGA Chevenard thermobalance which has been described previously.[3] For some combustion experiments of doped potassium chlorates with sulfur, a Moseley X-Y Recorder with a fast time base was connected to a Stone-Cahn Thermobalance.

The DTA experiments involving combustion of $KClO_3$-S mixed with oxides were done on IITRI designed DTA equipment[4] where thermocouples are placed in capillaries below the sample and reference material. Provisions are made for constant gas flows. Isothermal runs were performed on the Chevenard Thermobalance.

## C. Electrical Conductivity Experiments and Mass Spectrometric Analysis

Initial conductivity experiments were done in the conductivity cell described previously.[3] The cell was connected via a vacuum rack to a Bendix Time-of-Flight mass spectrometer to permit simultaneous conductivity measurements and mass spectrometric analysis.

This particular instrument configuration was later found to be impractical, since high background developed in the mass spectrometer due to the presence of stopcock grease in the vacuum rack. The conductivity cell has been redesigned to

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avoid these difficulties. Conductivity runs were performed separately in various gaseous atmospheres including water and sulfur vapor. Provisions were made for drying the gases over an activated bed of molecular sieves before they enter the conductivity cell.

Separate mass spectrometric analysis was initiated to investigate products formed during the reaction between doped $KClO_3$ and sulfur.

## D.    Additional Analytical Methods

Analyses were performed on the residues of low temperature isothermal experiments which took place over several days. $Cl^-$ was titrated according to the Mohr method. In a second sample $ClO_3^-$ was reduced by $Fe^{++}$. The $Cl^-$ content (from $Cl^- + ClO_3^-$) was again determined by the Mohr method. $ClO_3^-$ and $ClO_4^-$ were then reduced to $Cl^-$ by ignition with $NH_4Cl$, and again the overall $Cl^-$ content (from $Cl^-$, $ClO_3^-$ and $ClO_4^-$) determined by titration after Mohr. In order to check these results, $K^+$ was determined independently in a separate batch. Table 1 summarizes the results.

Analyses were also performed on initial crops of doped $KClO_3$ which were used in the thermal decomposition studies. Copper was colorimetrically determined with neocuproine, sodium by flame photometry and $Ca^{++}$ and $Ba^{++}$ were initially analyzed titrimetrically with EDTA against Eriochrome Black T. Poor reproducibility in the titration results for $Ca^{++}$ and $Ba^{++}$ due to the low concentrations present made it advisable to use a different indicator (Metab-Indicator) in order to check the rather low concentrations. Titration against Eriochrome

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## Table 1

## ANALYSIS OF $KClO_3$ REACTION PRODUCTS AFTER ISOTHERMAL

## DECOMPOSITION FOR SEVERAL DAYS AT 480°C

### Method

A. $Cl^-$                     -Mohr titration

B. $Cl^- + ClO_3^-$       -Reduction of $ClO_3^-$ with $Fe^{++}$, Mohr-titration of total $Cl^-$

C. $Cl^- + ClO_3^- + ClO_4^-$    -Reduction of $ClO_3^-$ and $ClO_4^-$ by ignition with $NH_4Cl$, Mohr titration of total $Cl^-$

Synthetic Sample: KCl - 0.852 meq; $KClO_3$ - 0.114 meq; $KClO_4$ - 0.913 meq.

### Analysis

| Analysis | Theoretical | Found |
|---|---|---|
| A. $Cl^-$ | 0.852 meq | 0.850 |
| B. $Cl^- + ClO_3^-$ | 0.967 meq | 0.977 |
| C. $Cl^- + ClO_3^- + ClO_4$ | 1.88 meq | 1.84 |

### Sample Under Investigation

| | | |
|---|---|---|
| $Cl^-$ | 0.748 meq/total sample = 55.8 mg KCl |
| $ClO_3^-$ | 0.071 meq/total sample = 8 7 mg $KClO_3$ |
| $ClO_4$ | 0.760 meq/total sample =105.4 mg $KClO_3$ |

                      1.579 meq               169.9 mg

                   Sample Wt. given 172.7 mg

$K^+$    61.2 mg

                 61.4 mg ± 0.2 mg

       61.6 mg

       61.4 mg = 1.57 ± 0.005 meq $K^+$

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Black T proved to be very difficult at low concentrations of Ca and at all concentrations of Ba, because the titration end point was rather difficult to detect. Tables 2 and 3 summarize the analytical results for $Na^+$, $Cu^{++}$, $Ba^{++}$ and $Ca^{++}$. Other auxiliary methods included x-ray analysis done with a Phillips X-ray diffractometer and microscopic investigations with a Zeiss polarizing microscope.

## III. EXPERIMENTAL RESULTS

### A. Analysis of Doped Samples of Potassium Chlorate

Potassium chlorate samples which were prepared by evaporating solutions of 1 mole % dopant with $KClO_3$ at 100°C to dryness were heterocrystalline; and with the exception of $FeCl_3$ and $CuCl_2$ doped samples, were white. Since the samples were obtained by way of evaporation, no analysis for the dopant content was necessary

A method for the preparation of doped single crystals was developed which involved evaporation of the solutions and crop collection in stages. Initial crops were analyzed for their dopant contents. The results are listed in Tables 2 and 3. Crops of crystals at higher concentrations were collected during the latter stages of the program.

The growth of the single crystals from water solutions was influenced by the amount and type of dopants. Large single crystals in the form of plates were obtained from solutions containing 0.1% or less of dopant.

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## Table 2

### EDTA TITRATION OF $KClO_3$ SINGLE CRYSTALS FOR Ca AND Ba AGAINST METALS AND/OR ERIOCHROME BLACK T INDICATORS

| Crop No. | % Dopant in Original Mother Liquid | % Dopant Against Metal | % Dopant Against Black Eriochrome |
|---|---|---|---|
| **Ca** | | | |
| 1.1 | 5% | -- | 0.0042 |
| 1.2 | 5% | 0.0064 | 0.0060 |
| 1.3 | 5% | -- | 0.0112 |
| 2.1 | 1% | 0.0020 | -- |
| 2.2 | 1% | 0.0037 | -- |
| 3.1 | 0.1% | 0.0007 | -- |
| 3.2 | 0.1% | 0.0017 | -- |
| **Ba** | | | |
| 1.1 | 5% | 0.0013 | |
| 1.2 | 5% | 0.0024 | |
| 1.3 | 5% | 0.0020 | |
| 2.1 | 1% | 0.0015 | |
| 3.1 | 0.1% | 0.0003 | |

## Table 3

ANALYSIS OF DOPED $KClO_3$ CROPS FOR $Na^+$ BY FLAME PHOTOMETRY, AND

FOR $Cu^+$ WITH NEOCUPROINE

| Sample | % Cu in Original Mother Liquid | % Cu |
|--------|-------------------------------|------|
| Crop #1 | 0.1% | 0.000086% |
| Crop #2 | 0.1% | 0.000086% |
| Crop #1 | 1% | 0.00018% |
| Crop #2 | 1% | 0.00014% |
| Crop #1 | 5% | 0.0069% |
| Crop #2 | 5% | 0.010% |
| Crop #3 | 5% | 0.0076% |

| Sample | % Na in Original Mother Liquid | % Na |
|--------|-------------------------------|------|
| Crop #1 | 0.1% | 0.0021% |
| Crop #2 | 0.1% | 0.0027% |
| Crop #1 | 1% | 0.0036% |
| Crop #2 | 1% | 0.0071% |
| Crop #1 | 5% | 0.0028% |
| Crop #2 | 5% | 0.0056% |
| Crop #3 | 5% | 0.0092% |

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If higher percentages of dopants were used the crystals were smaller in size. An exception was $NaClO_3$ where the single crystals formed in solutions of higher $NaClO_3$ concentrations were as large as the $KClO_3$ crystals. Observations with a polarizing microscope showed gross surface defects which are possibly due to etching by water during the washing process. Aside from this, structural defects were observed in some cases as judged from the birefringence pattern of the crystals under the crossed polarizer and analyzer of the microscope.

B.     X-Ray Analysis of Some Doped Samples of $KClO_3$

Attempts were made to analyze doped samples by X-ray, and investigate whether gross structural defects could be detected. No significant differences were observed which, in essence means that the different phases are too small to be detected or that the dopants were incorporated sub-stitutionally into the lattice. The exceptions are, perhaps the $LiNO_3$-doped sample which exhibit slightly lower intensities of the major peaks at a diffraction angle of about 20.9 and 21.8°, the lead nitrate-doped sample which shows additional lines and $CdCl_2$-doped samples which also show an additional peak.

C. _ _ . _ The Thermal Decomposition of $KClO_3$ at Low Temperatures

The low temperature isothermal decomposition studies of pure $KClO_3$ which were initiated during a previous program[3] were continued in order to obtain further insight into the disproportionation kinetics as the first stage of decomposition.

To this end, samples of undoped $KClO_3$ were isothermally decomposed at about 480°C. This reaction took place over several days. The final weight loss was approximately 33% of the overall weight loss at higher temperatures. The residue was analyzed as described in the experimental section. The results are summarized in Table 1. It may be seen that the mole percents of KCl and $KClO_4$ are approximately equal which is of significance for the proper interpretation of the overall decomposition reaction

D. The Decomposition of Potassium Chlorate in the Presence of Potassium Perchlorate

Mixtures of potassium chlorate and potassium perchlorate were prepared in the mole ratios, $KClO_4:KClO_3$ = 1:1 and 1:5. The purpose of these experiments was to investigate the possible catalytic influence of $KClO_4$ on the thermal decomposition of $KClO_3$. Some authors[5] deduced from isothermal experiments that $KClO_4$ catalyzes the isothermal decomposition of $KClO_3$. Unfortunately, their experiments were conducted with bare chromel-alumel thermocouples imbedded in the samples. Their experimental findings, therefore, must be considered unreliable since chromel-alumel thermocouples catalyze the thermal decomposition of both, potassium perchlorate[6] and potassium chlorate.[3]

Figure 1 shows the combined DTA/TGA curves of pure potassium chlorate, pure potassium perchlorate, and mixtures of potassium chlorate and potassium perchlorate in the mole ratios mentioned

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above. The total weights of the mixtures were adjusted in such a way that the overall weight loss was approximately the same for all samples. This permitted more direct comparisons between the weight loss curves.

The thermal stability of the mixture having a mole ratio of $KClO_4:KClO_3 = 1:5$ does not appear to differ appreciably from that of pure $KClO_3$ as indicated from the weight loss curves. The DTA curves for the mixture show a small endotherm at about 300°C due to the phase transition of the perchlorate. An increase in the relative amount of $KClO_4$ (Ratio 1:1) increases the magnitude of the transition endotherm and decreases the relative magnitude for the melting endotherm of $KClO_3$ at about 365°C. This double endotherm could be due to the formation of a eutectic between some reaction products and residual $KClO_3$. The higher the amount of $KClO_4$ in the mixture, the greater is the shift in the decomposition curves to higher temperatures. In addition, a sharp endotherm occurs at about 610°C where $KClO_4$ melts before it undergoes further decomposition.

E.    The Influence of the Final Decomposition Product, KCl, on the Thermal Decomposition of KClO$_3$

As in case of $KClO_4$, it is of importance to establish the role played by potassium chloride on the decomposition of $KClO_3$, since it is the final decomposition product.

It was observed during our previous program[3] that at sufficiently low temperatures chloride appeared to inhibit decomposition, but at higher temperatures it appeared to

Figure 1

DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRIC ANALYSIS OF PURE POTASSIUM CHLORATE AND MIXTURES OF POTASSIUM CHLORATE WITH POTASSIUM PERCHLORATE

$\Delta T$ (°C)

100

600

500

400

300

25
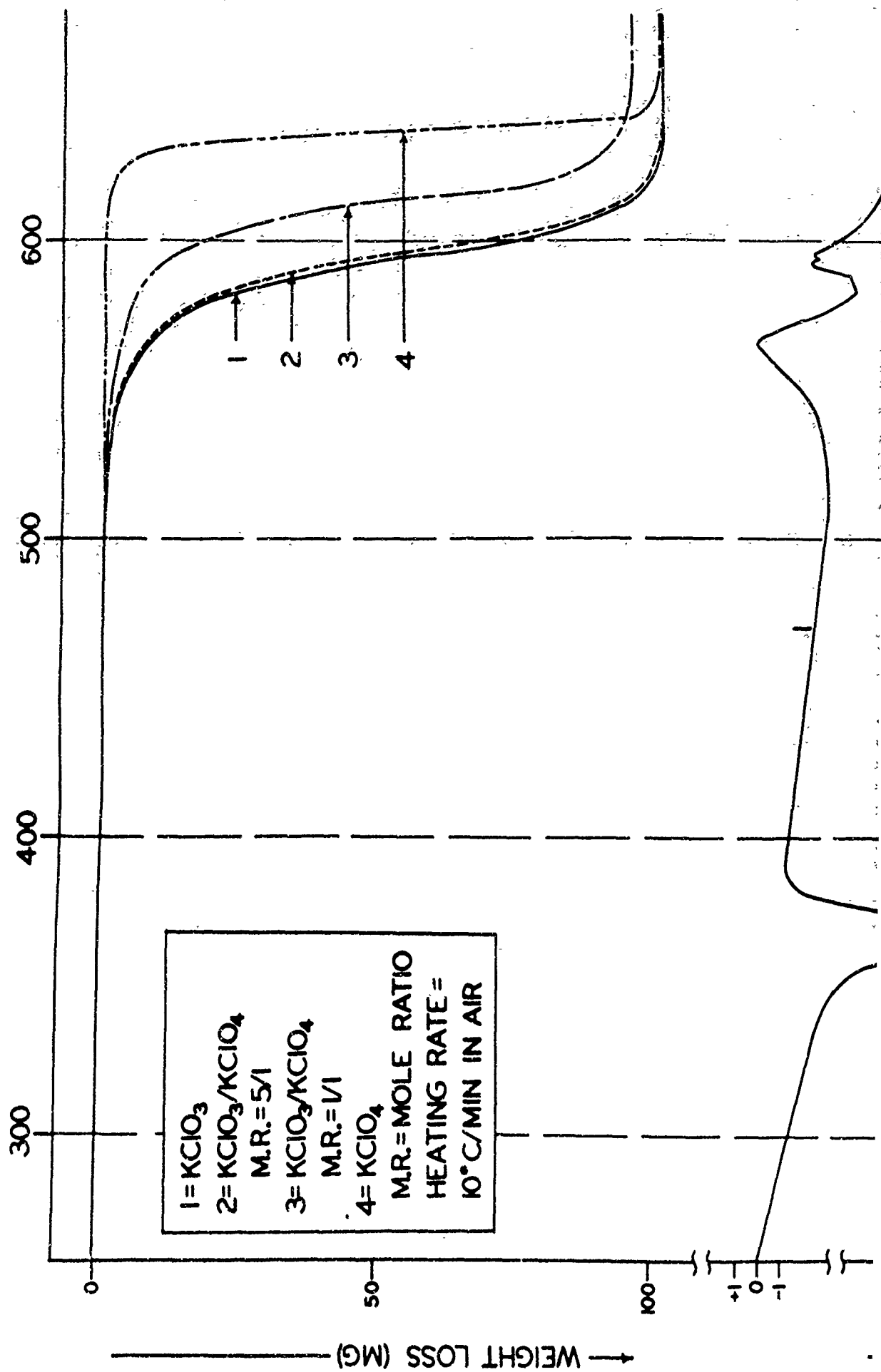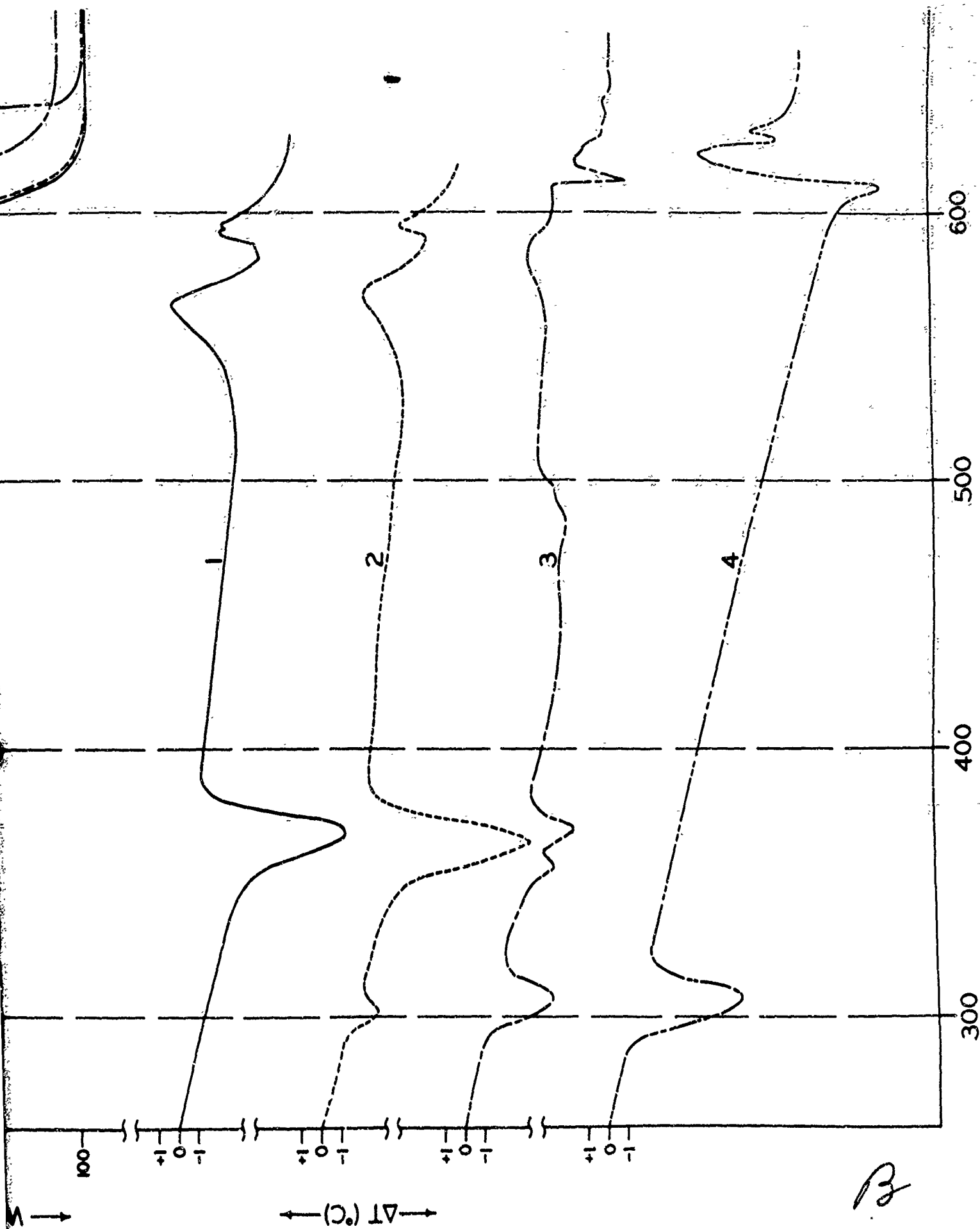
accelerate the reaction. Isothermal experiments were also carried out at temperatures below 500°C. It was found that at these low temperatures the decomposition mechanism of $KClO_3$ essentially involves complete disproportionation to KCl, $KClO_4$ and $O_2$. In addition, chloride was added to the $KClO_3$ in varying amounts so that the initial mixtures in the molten phase will vary in $KClO_3$ concentration. This is important because it was already demonstrated that chloride ion at sufficiently high concentrations as produced during the decomposition of $KClO_3$ can affect the rate of decomposition.

Figure 2 shows typical isothermal curves for the decomposition of undoped $KClO_3$ in varying concentrations with potassium chloride diluent. It is clearly seen that at sufficiently high concentrations of chloride the rate of decomposition is appreciably reduced in mixtures with chloride.

F. Effects of Doping on Chemical Reactivity

Thermogravimetric analysis and combination differential thermal analysis-thermogravimetric analysis experiments were performed on doped and undoped potassium chlorate. The combined DTA/TGA apparatus was described previously.[3] The heating rate was nominally 10 C per minute. Figure 3 shows comparisons of the thermal decomposition characteristics of pure $KClO_3$ with those of the doped materials. The results indicate that chloride salts did not appreciably influence its thermal decomposition characteristics. The chloride dopants included LiCl, KCl, and CsCl.

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Figure 2

INITIAL WEIGHT LOSS DURING ISOTHERMAL DECOMPOSITION OF PURE $KClO_3$
AND IN MIXTURES WITH KCl
(Temperature About 480°C)
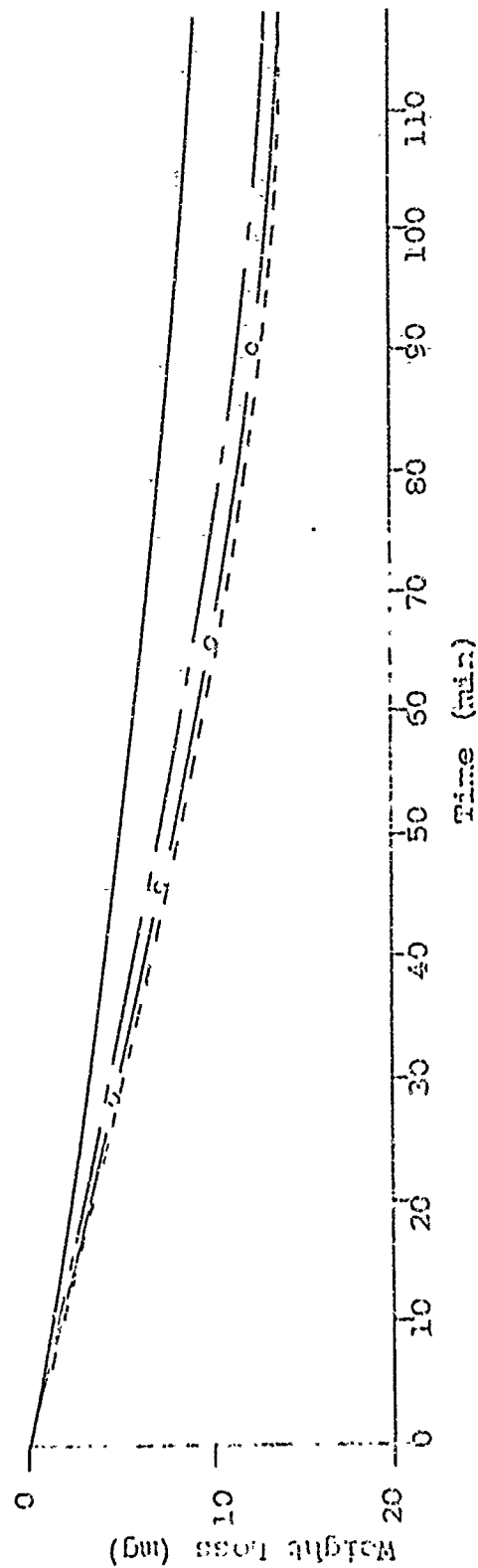


| Symbol | Mole Ratio $KCl/KClO_3$ |
|--------|--------------------------|
| ⎯⎯⎯ | 1:1 |
| — — — | 1:2 |
| —○— | 1:3 |
| – – – | 0:1 |

# Figure 3

## THERMOGRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS OF DOPED POTASSIUM CHLORATES

DOPANTS
1 = $FeCl_3 \cdot 6H_2O$
2 = $CuCl_2 \cdot 2H_2O$
3 = $Pb(NO_3)_2$
4 = $LiNO_3$
5 = $CaCl_2$
6 = $CdCl_2 \cdot 2\,1/2H_2O$
7 = $KCl$
8 = $LiCl$
9 = $CsCl$
10 = NONE

AMOUNT OF DOPANTS : 1 MOLE %
HEATING RATE : 10°C MIN
SAMPLE SIZE : 200 MG
ATMOSPHERE : AIR

WEIGHT LOSS (MG)

TEMPERATURE (°C) —→

ΔT (°C)

3
4
5
6
7
8
9
10

300    400    500    600

31
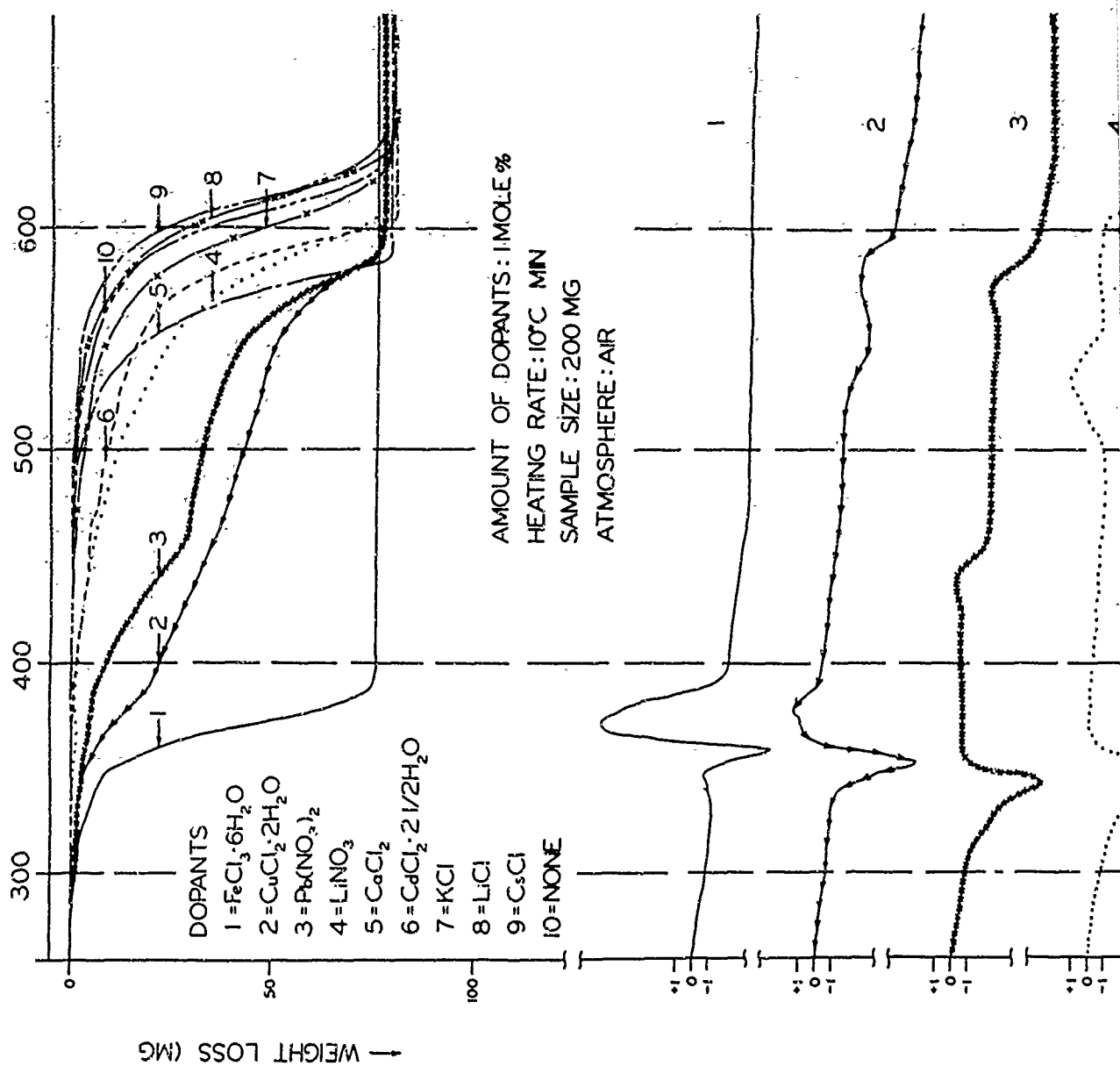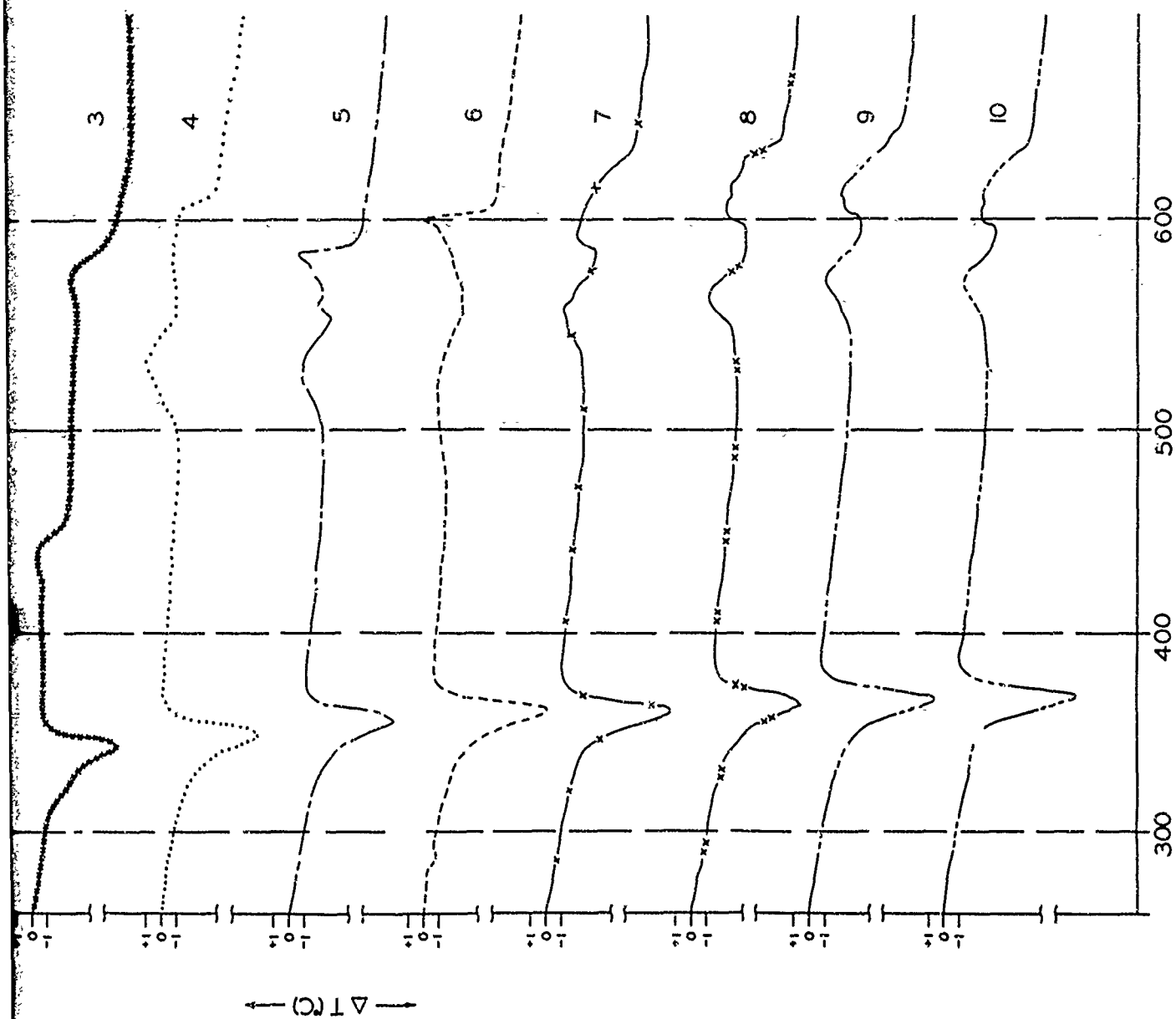
The data based on the experiments are tabulated in Table 4 and reveal several interesting points.

1. The average temperatures of the endothermal minimum at the melting point of $KClO_3$ are only slightly decreased upon addition of chloride. The decreases in temperature is much more pronounced upon addition of the nitrate impurities.

2. Doping with the nitrates has the effect of decreasing the average decomposition temperatures from 25° to 50' below the temperatures of decomposition of the pure and chloride doped chlorates.

3. The most effective dopants are $FeCl_3$ and $CuCl_2$. In particular, doping with $FeCl_3$ causes appreciable thermal decomposition of $KClO_3$ to occur below the temperature of the melting endotherm as is seen in Figure 3.

In Figure 4 the effect of cation doping on the thermal characteristics of doped single crystals is demonstrated. It is seen that dopants such as $Na^+$ and $Ba^{++}$ have, if at all, only little influence on the thermal decomposition characteristics of $KClO_3$. Even crystals which were crystallized from solutions containing 10% $Na^+$ (which coincides with the curve obtained from 1% $Na^+$), and 10% $Ba^{++}$ do not differ appreciably in their thermal behavior from the undoped material. In case of $Na^+$ this is not unexpected, since $Na^+$ is in the same group of the periodic system as $K^+$. The decomposition behavior of 10% $Ca^{++}$ doped $KClO_3$ is significantly different from the behavior of pure $KClO_3$. The most pronounced differences in thermal
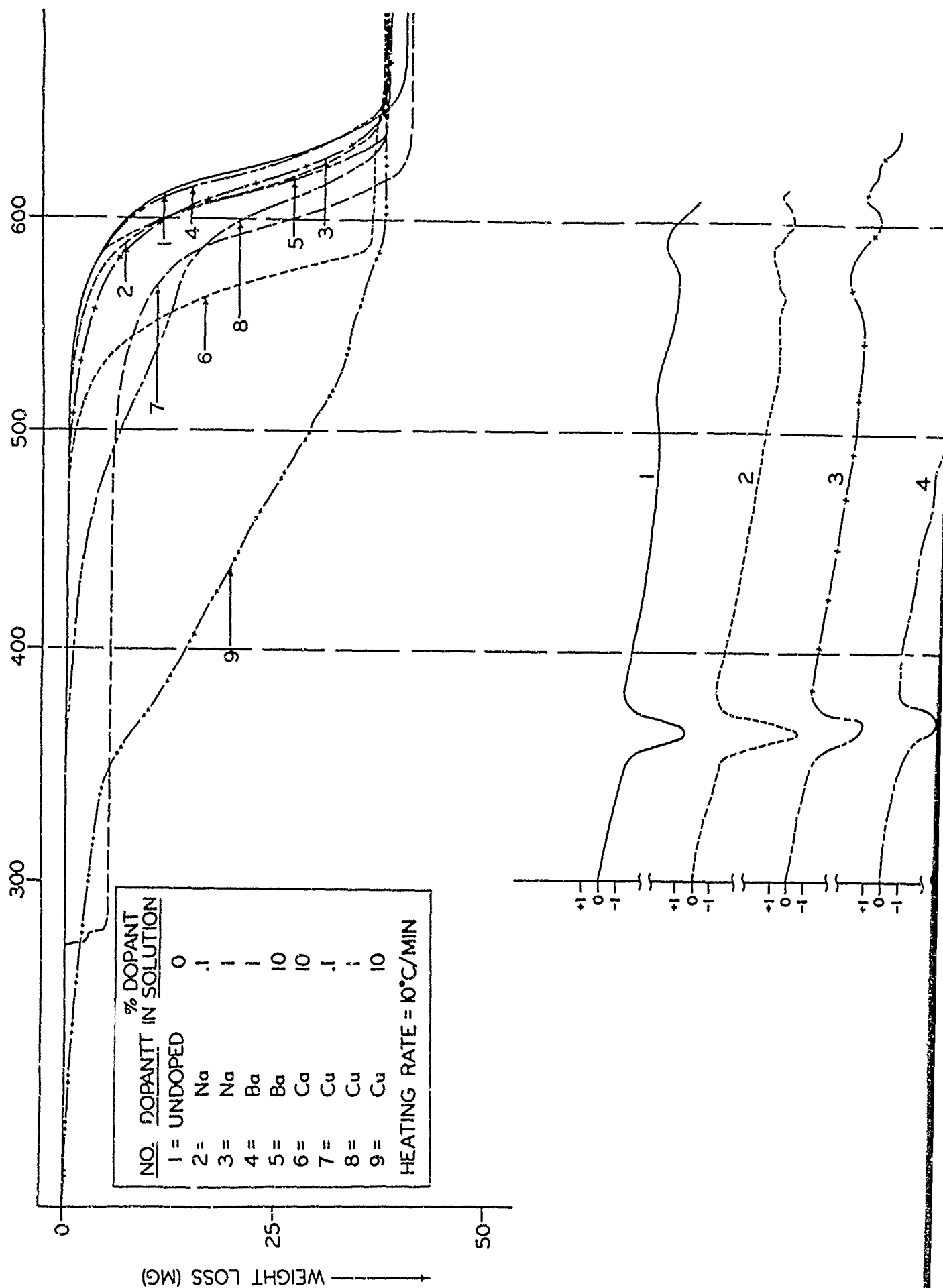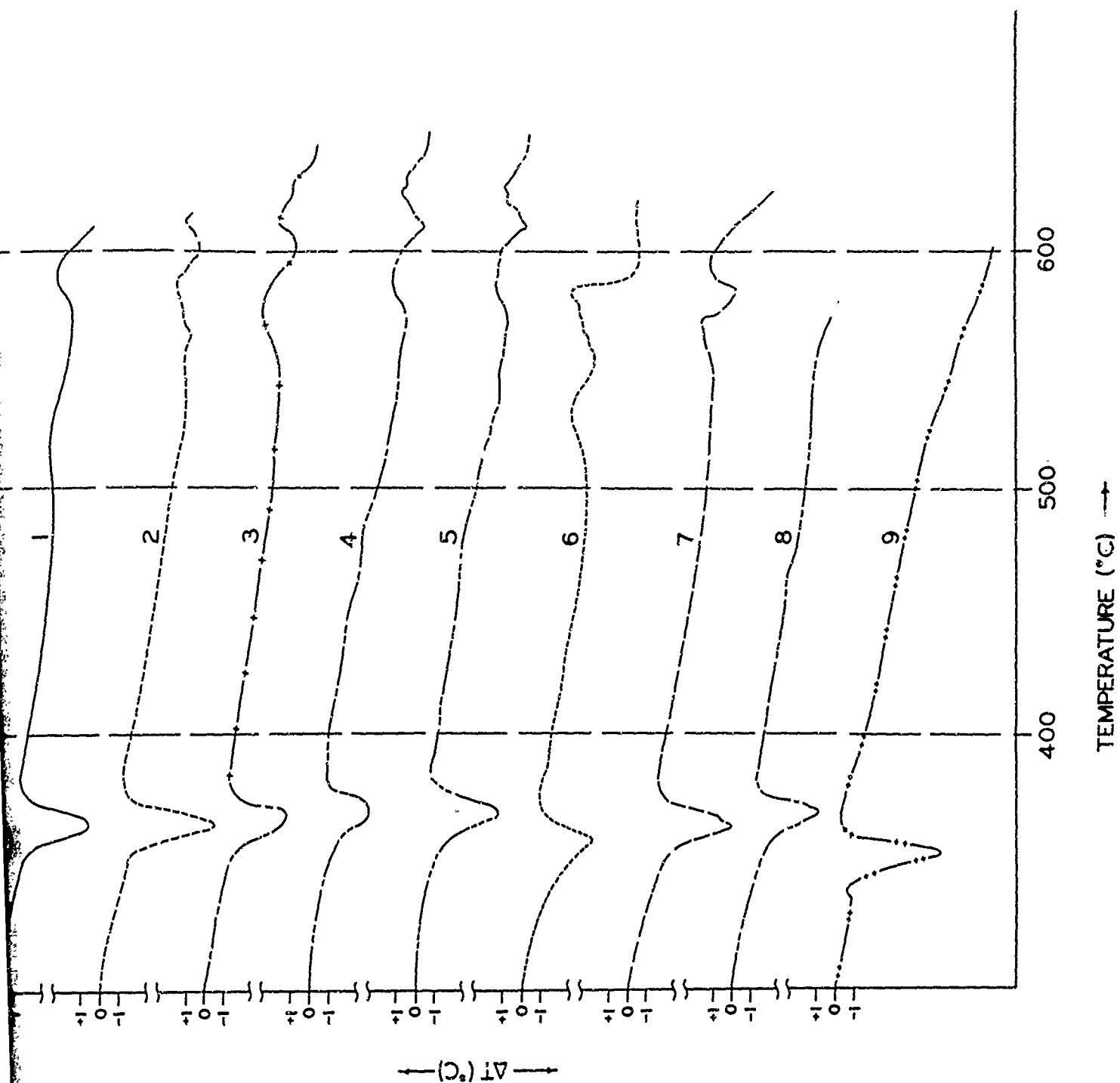
Table 4

SUMMARY OF THERMAL ANALYSIS RESULTS

| Dopant | Average Peak Endothermal Temperature | Average Decomposition Temperature at 25% wt Loss | Average Decomposition Temperature at 50% wt loss | Charge Density of Cationic Dopant Electrons/$Å^2$ |
|---|---|---|---|---|
| LiCl | 363 $\pm$ 2.6 | 588.7 $\pm$ 8.1 | 607.3 $\pm$ 2.6 | 0.69 |
| KCl | 360 $\pm$ 0.0 | 581.5 $\pm$ 2.1 | 606.5 $\pm$ 0.7 | 0.179 |
| CsCl | 367.7 $\pm$ 2.5 | 601.7 $\pm$ 7.6 | 618 $\pm$ 5.3 | 0.114 |
| $CuCl_2$ | 353.3 $\pm$ 1.5 | 398.3 $\pm$ 2.9 | 485 $\pm$ 5.0 | 1.240 |
| $CdCl_2$ | 360.7 $\pm$ 9.3 | 562.3 $\pm$ 6.8 | 586 $\pm$ 7.9 | 0.678 |
| $CaCl_2$ | 355.3 $\pm$ 19.6 | 554.3 $\pm$ 14.3 | 568.3 $\pm$ 12.8 | 0.650 |
| $FeCl_3$ | 357.5 $\pm$ 3.5 | 354 $\pm$ 1.4` | 375 $\pm$ 0.0 | 2.42 |
| $Pb(NO_3)_2$ | 342.5 $\pm$ 0.7 | 441.5 $\pm$ 0.7 | 543.5 $\pm$ 9.2 | 0.442(1.800)[*] |
| $Li(NO_3)$ | 349 $\pm$ 15.5 | 549 $\pm$ 8.5 | 585 $\pm$ 7.1 | 0.69 |
| NONE | 368 $\pm$ 4.2 | 606.5 $\pm$ 2.1 | 620 $\pm$ 2.8 | 0.0 |

[*]Second number refers to four-valent lead

Figure 4

THE EFFECT OF CATION DOPING ON THE THERMAL CHARACTERISTICS OF SINGLE CRYSTALS



| NO. | DOPANT | % DOPANT IN SOLUTION |
|-----|--------|----------------------|
| 1 = | UNDOPED | 0 |
| 2 = | Na | .1 |
| 3 = | Na | — |
| 4 = | Ba | .1 |
| 5 = | Ba | 10 |
| 6 = | Ca | 10 |
| 7 = | Cu | .1 |
| 8 = | Cu | — |
| 9 = | Cu | 10 |

HEATING RATE = 10°C/MIN

WEIGHT LOSS (MG)

TEMPERATURE (°C) ⟶

⟵ ΔT (°C) ⟶

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characteristics are found, if the solutions were doped with .1, 1, and 10% $Cu^{++}$. The single crystals obtained from 10% solutions were most reactive. Slow decomposition begins much below the melting point of $KClO_3$ and the melting point is shifted towards lower temperatures. At least two steps are seen in the weight loss curves of $Cu^{++}$ doped $KClO_3$. Initial weight loss of the sample doped with 0.1 $Cu^{++}$ occurs below 300°C.

## G. The Effect of Gamma-Irradiation and Mechanical Shock on the Thermal Decomposition of $KClO_3$

Experiments were initiated to elucidate possible effects of irradiation and mechanical shock on the thermal decomposition of potassium chlorate. The results are very interesting. It was observed that the data appeared to be poorly reproducible, if time and atmospheric conditions during storage were not kept under very careful control. If the irradiated samples were taken directly from the hot cell, a chlorine odor was discernible, and the samples were of tannish color. If the samples were dried at about 110°C, the color faded and the smell disappeared.

A DTA/TGA experiment on a sample placed on the thermobalance immediately after it was taken from the hot cell, showed exothermal and endothermal decomposition steps at low temperatures. Partial weight loss is observed at ambient temperatures (Figure 5). This low temperature weight loss is approximately 18.5% of the total weight. The total weight loss after complete decomposition is approximately 60%.

If the sample is dried in a desiccator or if it is stored
for a longer period of time, the low temperature weight loss
is no longer observable. A sample dried in an oven at 110°C
looses its tannish color and again, low temperature weight
loss is no longer apparent. The melting endotherm of irradiated
$KClO_3$ shows two pronounced shoulders, while the higher tem-
perature exotherms appear similar to those of unirradiated
material. One sample of $KClO_3$ which had been subjected to
mechanical shock showed a similar but smaller weight loss
at low temperatures as the irradiated material directly after
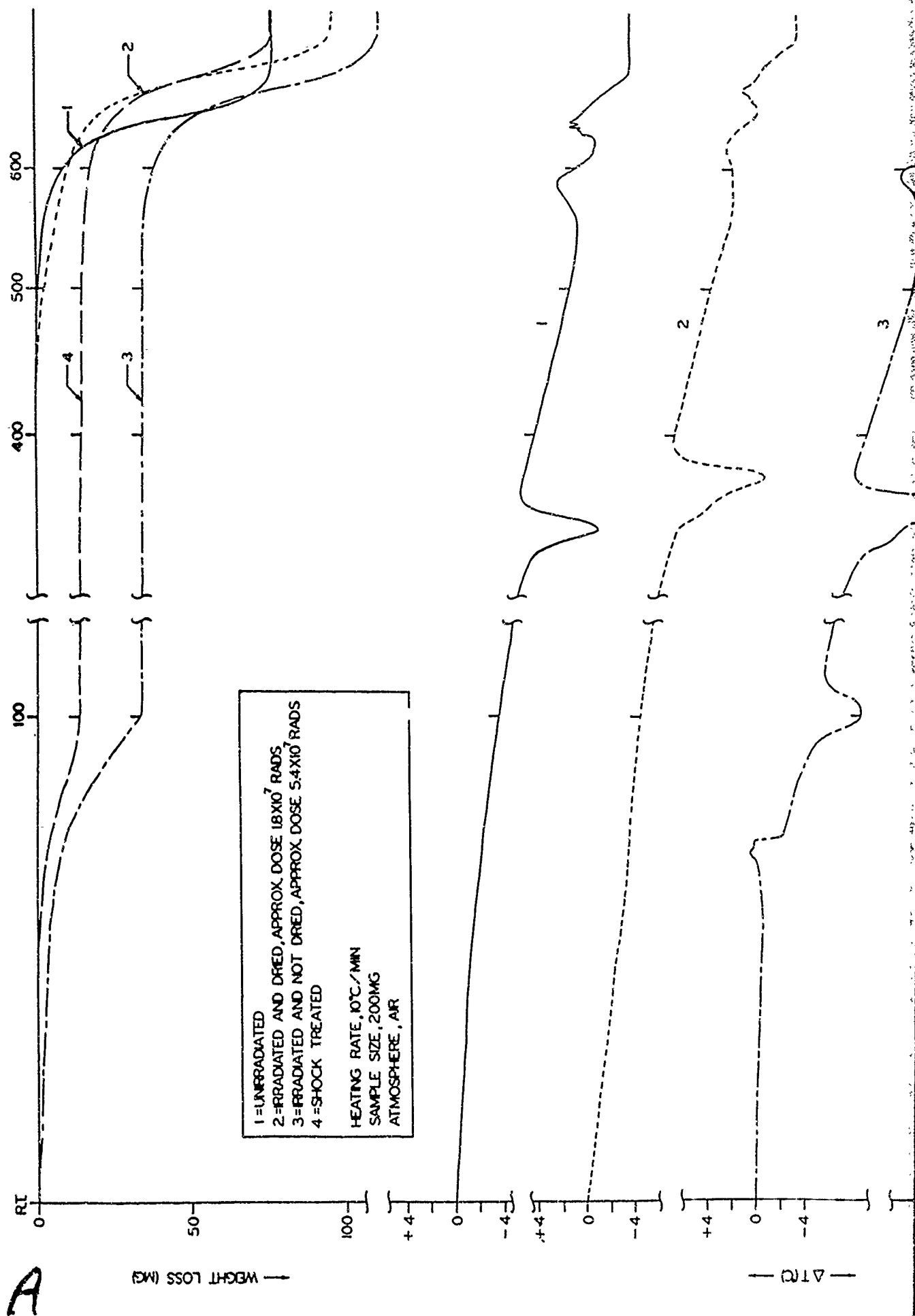irradiation. (Figure 5).

## H. Electrical Conductivity Studies and Mass Spectrometric Analysis of Potassium Chlorate

Preliminary electrical conductivity experiments were
started to test the conductivity cell which was set up in
conjunction with a Bendix Time-of-Flight mass spectrometer.
This has the advantage of combining the electrical conductivity
setup with a sensitive analytical tool to determine the gaseous
reaction products. $KClO_3$ was pressed at 20,000 psi to form a
cylindrical pellet. The opposite surfaces were ground parallel
to provide for smooth contact with the platinum electrodes of
the conductivity cell.

Figure 6 shows electrical conductance curves of undoped
$KClO_3$ in air at atmospheric pressure and in vacuum at less
than $10^4$ mm Hg. The sample was heated at a constant rate of
about 10' C/min. The logarithm of the electrical conductance

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Figure 5

INFLUENCE OF IRRADIATION AND MECHANICAL SHOCK ON THE DECOMPOSITION OF POTASSIUM CHLORATE



1 = UNIRRADIATED
2 = IRRADIATED AND DRIED, APPROX DOSE 1.8X10$^7$ RADS
3 = IRRADIATED AND NOT DRIED, APPROX DOSE 5.4X10$^7$ RADS
4 = SHOCK TREATED

HEATING RATE, 10°C./MIN
SAMPLE SIZE, 200MG
ATMOSPHERE, AIR

HEATING RATE, 10°C/MIN
SAMPLE SIZE, 200MG
ATMOSPHERE, AIR

100

+4
0
-4

+4
0
-4

+4
0
-4

+4
0
-4

R.T

ΔT(°C)
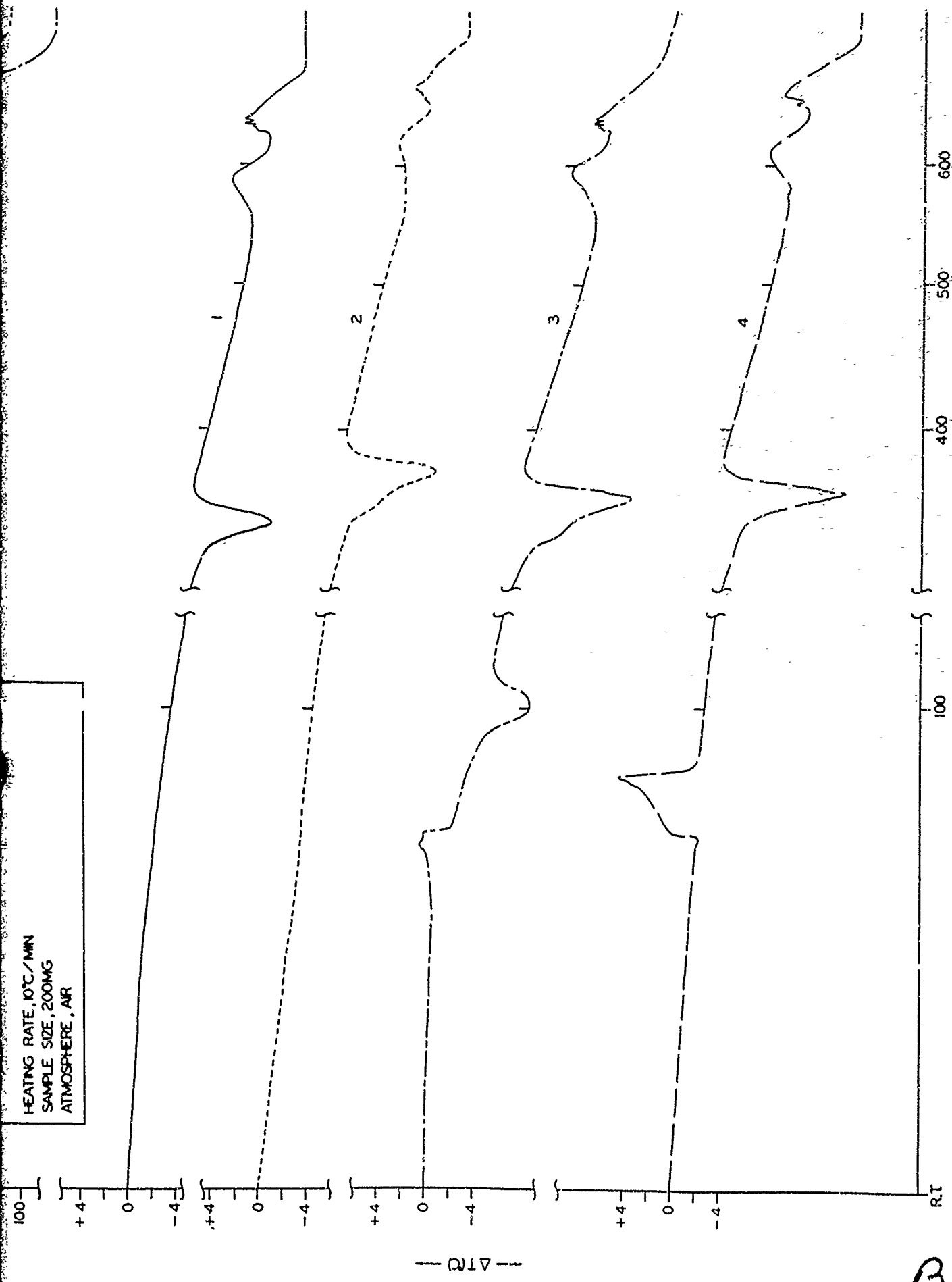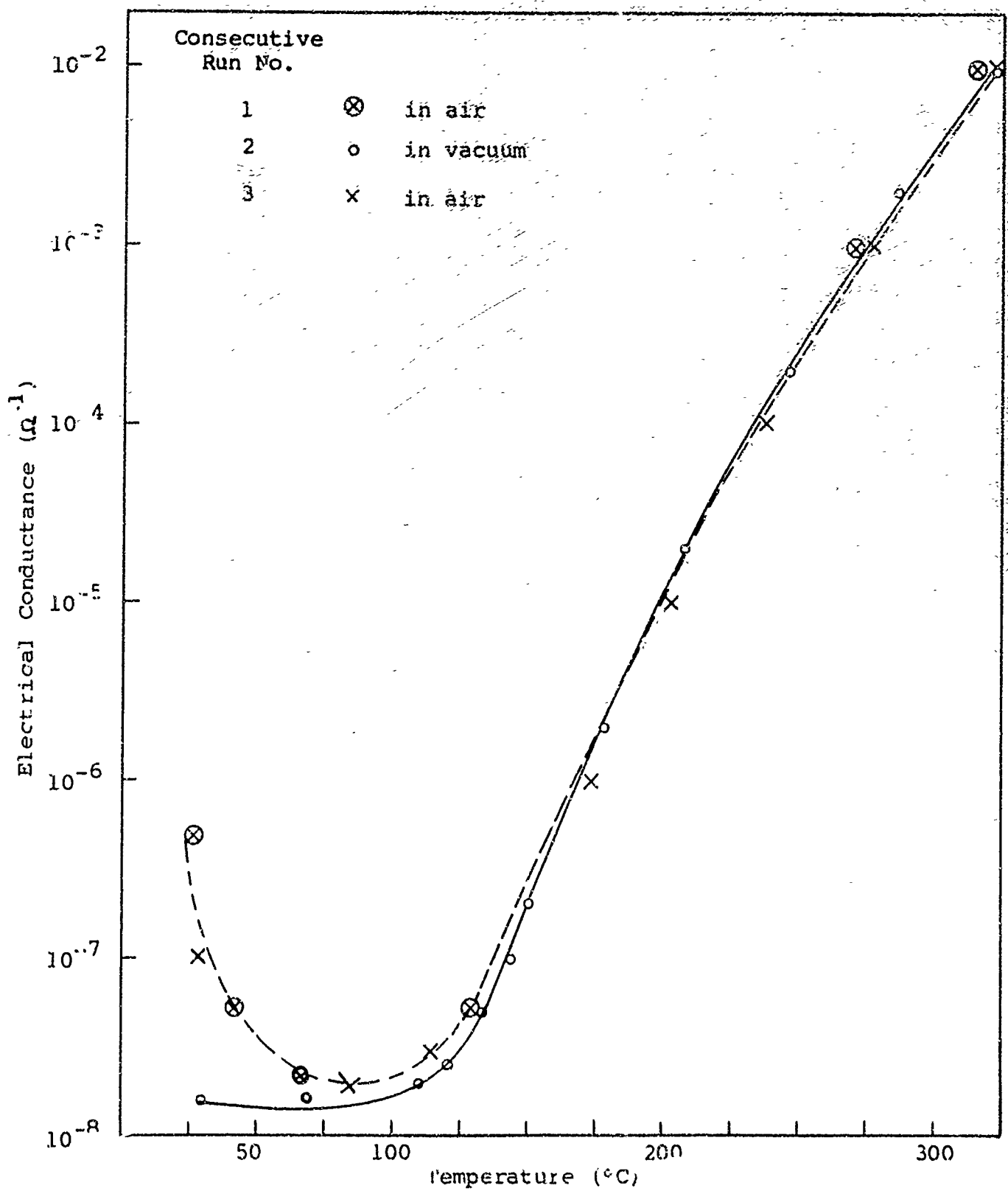
TEMPERATURE (°C) ⟶

100    400    500    600

1

2

3

4

39

Figure 6

ELECTRICAL CONDUCTANCE OF A $KClO_3$ PELLET

is plotted as a function of the temperature. This data is
taken directly from the recorded curves. It is seen that
the conductance is similar at temperatures above 150°C for
the sample in air and in vacuum. At lower temperatures,
however, the sample in air increases in conductivity with
decreasing temperatures. This is not true under vacuum where
the conductivity continues to decrease as the temperature
is reduced.

In Figure 7 the conductivity is plotted as a function
of inverse absolute temperature. The activation energy
obtained from the straight portions of these curves is about
32 kcal/mole.

Conductivity runs were also performed in various gas
and vapor atmospheres. The results are summarized in Figure 8.
It can be seen that water vapor significantly increases the
electrical conductivity at low temperatures which explains the
fact that preliminary runs (Figure 6) in undried air were found
to be non-reproducible at low temperatures. The electrical con-
ductivity in dry oxygen, argon and in air does not appear to be
significantly different from the conductivity in vacuum. It
was, however, observed that the steady state pressure in the
system increases from a value of $10^{-5}$ at room temperature to
$10^{-3}$ mm Hg at temperatures above 300°C in vacuum. Preliminary
attempts of simultaneous mass spectrometric analysis failed,
because of a large background problem.

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Figure 7

ACTIVATION ENERGY OF THE CHARGE TRANSFER
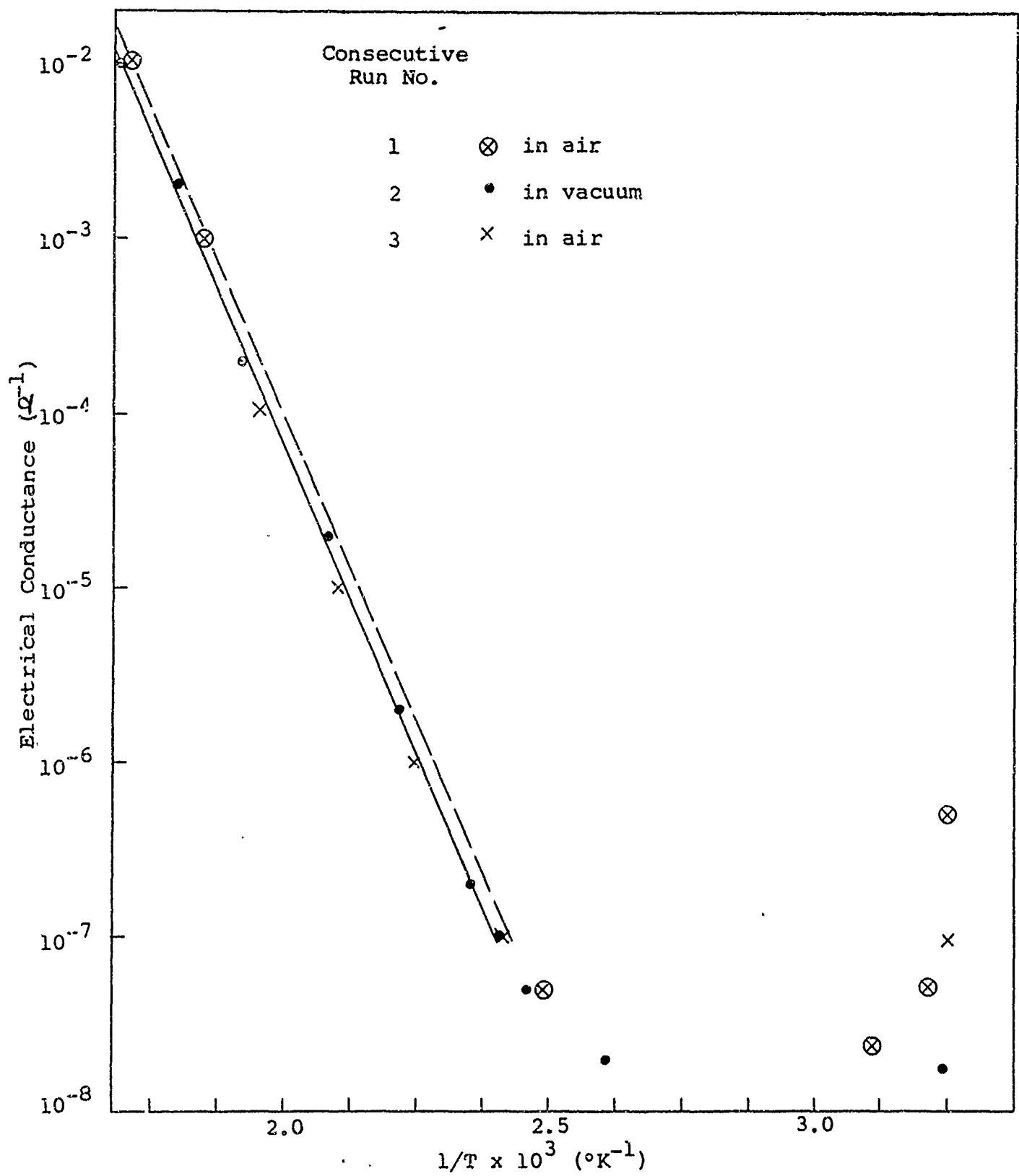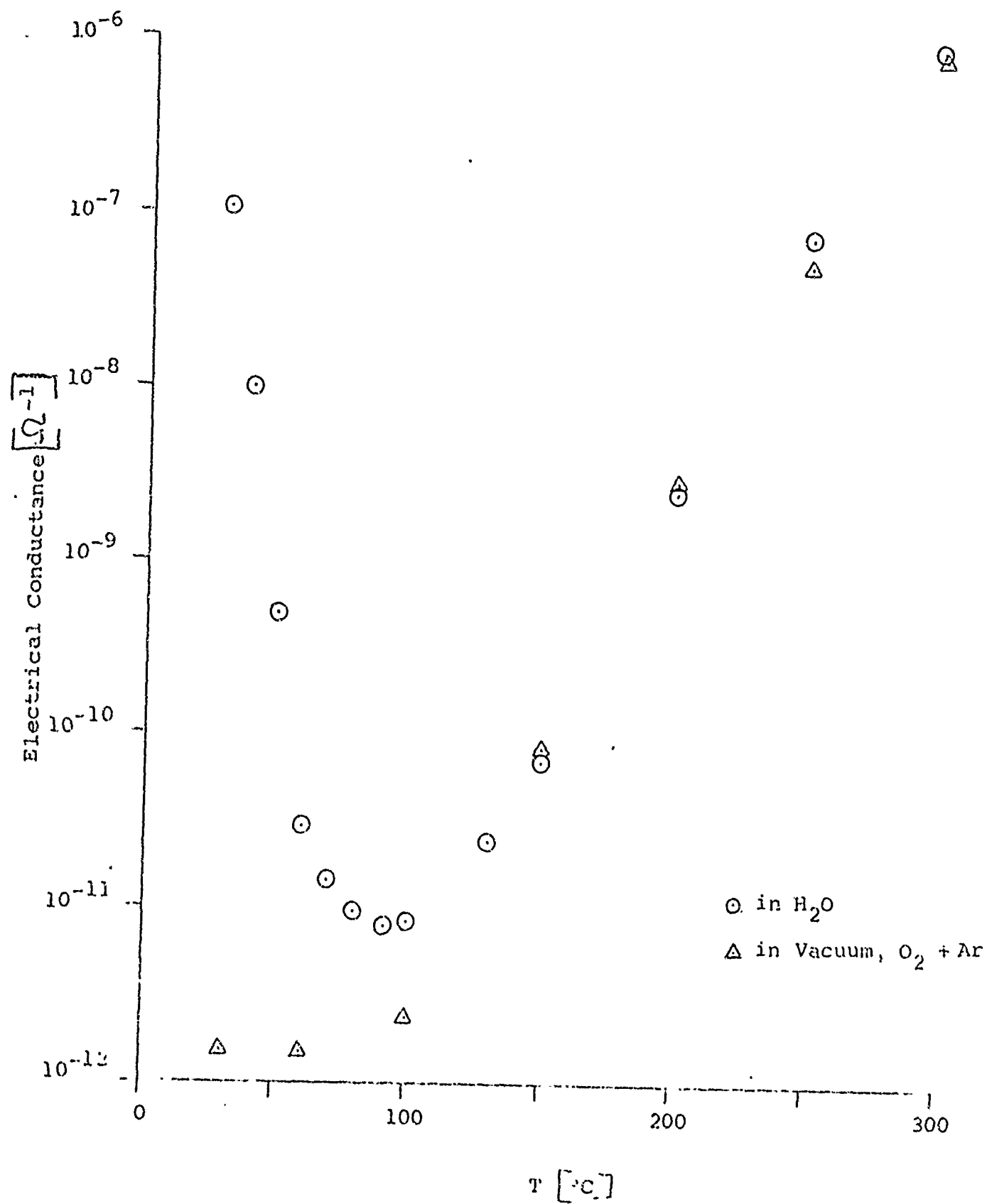IN A POTASSIUM CHLORATE PELLET

Figure 8

INFLUENCE OF WATER VAPOR ON THE ELECTRICAL CONDUCTIVITY OF
POTASSIUM CHLORATE

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## I. Thermal Analysis of the Combustion of Doped $KClO_3$ in Mixtures with Sulfur

Preliminary DTA/TGA runs were carried out with various mixtures of sulfur and doped potassium chlorates. The potassium chlorate samples were obtained from evaporation of 1% dopant in $KClO_3$ solutions. This was done to investigate the influence of doped $KClO_3$ on the combustion of sulfur.

Table 5 summarizes the results in terms of ignition temperature. The average values of the ignition temperatures and corresponding error limits (standard deviations from these values) are compiled in Table 6. The ignition temperature is lowest with $KClO_3$ doped with 1% $CuCl_2$. It is reduced by more than 20°C as compared to the ignition temperature of the undoped chlorate. McLain[7] also showed similar results for $Cu^{++}$ doped mixtures. The effect of the dopants on the ignition temperature is $CuCl_2 \sim KCl \sim$ Undoped $\sim CsCl \sim Pb(NO_3)_2 < FeCl_3 \approx CdCl_2 < LiCl \sim LiIO_3 \sim CaCl_2$. It is interesting to note that $FeCl_3$ is much less active as far as the ignition temperature is concerned than $CuCl_2$. It should, however, be pointed out that the average weight loss is much higher with $FeCl_3$ than with all the other dopants. The stoichiometric weight loss according to the equation:

$$2KClO_3 + 3S = 2KCl + 3SO_2$$

is approximately 37.6%. The actual weight losses are much higher.

Therefore, the observed weight losses are significant only in that they showed a more vigorous reaction is taking place in the $FeCl_3$ doped reaction.

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# Table 5

## THE COMBUSTION OF SULFUR WITH DOPED SAMPLES OF POTASSIUM CHLORATE

| 1 mole % Dopant | Ignition Temperature (°C) |
|---|---|
| Undoped | 142 |
| Undoped | 141 |
| Undoped | 137 |
| $FeCl_3$ | 142 |
| $FeCl_3$ | 145 |
| $CuCl_2$ | 118 |
| $CuCl_2$ | 120 |
| CsCl | 138 |
| CsCl | 142 |
| $LiNO_3$ | 150 |
| $LiNO_3$ | 155 |
| LiCl | 150 |
| LiCl | 151 |
| $Pb(NO_3)_2$ | 145 |
| $Pb(NO_3)_2$ | 137 |
| $Pb(NO_3)_2$ | 140 |
| $Pb(NO_3)_2$ | 138 |
| KCl | 137 |
| KCl | 142 |
| $CdCl_2$ | 143 |
| $CdCl_2$ | 147 |
| $CaCl_2$ | 155 |
| $CaCl_2$ | 147 |

## Table 6

### AVERAGE IGNITION TEMPERATURES FOR THE REACTION OF SULFUR WITH DOPED POTASSIUM CHLORATES

| Dopant | Average Ignition Temperature (°C) |
|---|---|
| Undoped | $140 \pm 2.2$ |
| $FeCl_3$ | $143.5 \pm 2.1$ |
| $CuCl_2$ | $119 \pm 1.4$ |
| CsCl | $140 \pm 2.8$ |
| $LiNO_3$ | $152.5 \pm 3.5$ |
| LiCl | $150.5 \pm 0.7$ |
| $Pb(NO_3)_2$ | $140 \pm 3.1$ |
| KCl | $139.5 \pm 3.5$ |
| $CdCl_2$ | $145 \pm 2.8$ |
| $CaCl_2$ | $151 \pm 5.7$ |

TGA runs were performed using a relatively fast x-y-recorder to elucidate the rates of combustion in $KClO_3$-S mixtures with and without additional $KClO_3$ as diluents, the results indicated that the rate of combustion even in dilute mixtures is too fast to be determined by the x-y-recorder.

J.   Catalytic Activity of Metal Oxides on the Ignition of Potassium Chlorate-Sulfur Mixtures

The influence of metal oxide additives on the combustion of mixtures of potassium chlorate and sulfur was probed by differential thermal analysis. The oxides considered were $Fe_2O_3$, $Cr_2O_3$, and $Al_2O_3$. These oxides were selected since the first two were found to be excellent catalysts while $Al_2O_3$ was relatively inactive. The concentration of the oxides were varied from 5 to 50 mole percent. These runs were generally performed in an argon atmosphere. A few experiments were carried out in an oxygen atmosphere. In an argon atmosphere the possibility of air oxidation is eliminated thereby limiting the oxidation of sulfur to reaction with the $KClO_3$ in the mixture. Carrying out the reaction in pure oxygen emphasizes the role of air oxidation in the combustion reaction. Table 7 shows the results. It can be seen that the ignition temperature differs significantly depending on the mole ratio of metal oxide to potassium chlorate and is also dependent on the gaseous environment. In Figure 9 the peak temperatures of the ignition exotherms are plotted as a function of mole ratio of the metal oxide to potassium chlorate.

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## Table 7

### COMBUSTION OF SULFUR-POTASSIUM CHLORATE IN MIXTURES WITH OXIDE CATALYSTS

| Catalyst | Atmosphere | Mole Ratio | Ignition Temperature | Relative Peak Height | Remarks |
|----------|-----------|-----------|---------------------|---------------------|---------|
| $Fe_2O_3$ | Ar | 1:10 | 157 | 3.25 | |
| $Fe_2O_3$ | Ar | 1:10 | 158 | 2.20 | |
| $Fe_2O_3$ | Ar | 3:10 | 164 | >2.9 | off chart |
| $Fe_2O_3$ | Ar | 3:10 | 162 | 1.6 | |
| $Fe_2O_3$ | Ar | 1:20 | 186 | 2.0 | |
| $Fe_2O_3$ | Ar | 1:20 | 190 | 0.2 | 2S |
| $Fe_2O_3$ | Ar | 1:20 | 191 | 0.7 | |
| $Al_2O_3$ | Ar | 1:10 | 163 | 2.8 | |
| $Al_2O_3$ | Ar | 1:10 | 170 | 3.6 | |
| $Cr_2O_3$ | Ar | 1:10 | 173 | | |
| $Cr_2O_3$ | Ar | 1:10 | 170 | 0.7 | |
| $Cr_2O_3$ | $O_2$ | 1:10 | 157 | | |
| $Fe_2O_3$ | $O_2$ | 1:10 | 154 | >3 | off chart |

Heating Rate: 10°C/min

Amount $KClO_3$: 200 mg

Amount Sulfur: 75 mg ( except 2S = 150 mg)

Gas Flow: 300 ml/min

## Table 7

### COMBUSTION OF SULFUR-POTASSIUM CHLORATE IN MIXTURES WITH OXIDE CATALYSTS

| Catalyst | Atmosphere | Mole Ratio | Ignition Temperature | Relative Peak Height | Remarks |
|----------|------------|------------|----------------------|----------------------|---------|
| $Fe_2O_3$ | Ar | 1:10 | 157 | 3.25 | |
| $Fe_2O_3$ | Ar | 1:10 | 158 | 2.20 | |
| $Fe_2O_3$ | Ar | 3:10 | 164 | >2.9 | off chart |
| $Fe_2O_3$ | Ar | 3:10 | 162 | 1.6 | |
| $Fe_2O_3$ | Ar | 1:20 | 186 | 2.0 | |
| $Fe_2O_3$ | Ar | 1:20 | 190 | 0.2 | } 2S |
| $Fe_2O_3$ | Ar | 1:20 | 191 | 0.7 | |
| $Al_2O_3$ | Ar | 1:10 | 163 | 2.8 | |
| $Al_2O_3$ | Ar | 1:10 | 170 | 3.6 | |
| $Cr_2O_3$ | Ar | 1:10 | 173 | | |
| $Cr_2O_3$ | Ar | 1:10 | 170 | 0.7 | |
| $Cr_2O_3$ | $O_2$ | 1:10 | 157 | | |
| $Fe_2O_3$ | $O_2$ | 1:10 | 154 | >3 | off chart |

Heating Rate: 10°C/min

Amount $KClO_3$: 200 mg

Amount Sulfur: 75 mg ( except 2S = 150 mg)

Gas Flow: 300 ml/min

It should be pointed out that there was a rather wide spread of experimental points, and therefore, only general trends can be discussed. Additional experiments would possibly result in data with improved precision. Because of the limited effort most of the work was confined by $Fe_2O_3$. If one considers the general trend of the results with the $Fe_2O_3$ additive, as the concentration is increased from zero to 5 mole % oxide the principle effect is an increase in the ignition temperature. As additional $Fe_2O_3$ oxide is added and the optimum ratio for catalytic activity is approached there is a minimum in the ignition temperature curve which represents the maximum lowering of the ignition temperature. This occurs at the mole ratio of oxide to $KClO_3$ of 1/10. There is again an increase in ignition temperature at higher concentrations of oxide. It appears, however, that $Al_2O_3$ and $Cr_2O_3$ are significantly less active than ferric oxide at the 1/10 mole ratio. On the other hand, it may be noted that in oxygen the ignition temperature of the mixture containing $Cr_2O_3$ was appreciably reduced, and was comparable to the $Fe_2O_3$ containing compositions. There was also a slight decrease in the ignition temperature of the mixture containing $Fe_2O_3$ in the presence of oxygen. At the mole ratio of 3/10 oxide in $KClO_3$ it is seen that an increase in concentration of sulfur from stoichiometric to double the stoichiometric amount results in a lower ignition temperature In summary the most significant findings appear to be those for the compositions containing the $Fe_2O_3$ catalyst where a minimum in the ignition temperature curve occurs at the mole ratio of oxide to $KClO_3$ of 1/10

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## IV.  DISCUSSION

### A.  Mechanism of the Decomposition of Potassium Chlorate

It was tentatively concluded at the termination of our previous investigation[3] that the initial disproportionation step during decomposition of $KClO_3$ involves apparently a direct oxygen transfer between two $ClO_3^-$ anions.

$$\begin{bmatrix} O \\ Cl\text{-}O \\ O \end{bmatrix}^- + \begin{bmatrix} O \\ ClO \\ O \end{bmatrix}^- \longrightarrow \begin{bmatrix} O \\ O\text{-}Cl\text{-}O \\ O \end{bmatrix}^- + \begin{bmatrix} O \\ Cl \\ O \end{bmatrix}^-$$
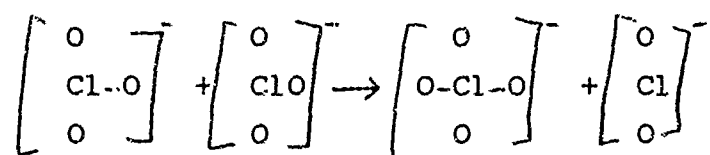
This was born out by the observations that the extrapolated initial weight loss was found to be approximately 33% of the total weight loss (See Figure 35 of Ref. 3) and that the relative amounts in the residues are approximately 50 mole % $KClO_4$ and 50 mole % KCl at the inflection point of the weight loss curve of $KClO_3$. In order to obtain further evidence, isotherms were performed at low temperatures, where decomposition of $KClO_4$ is negligible, and the order of reaction evaluated. In Figure 10, isothermal data at 480°C are plotted in first and second order plots, and in Figure 11 log dw/dt is plotted versus log $W_r$. The first figure indicates that the second order plot is approximately descriptive of the mechanism, while the slope (as a measure of the order) of the second graph is evaluated to be about 2.3. Additional evidence for the disproportionation reaction is found in Table 3 which indicates that the low temperature reaction yields approximately the same moles of KCl and $KClO_4$.

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Figure 10

FIRST AND SECOND ORDER PLOT OF $KClO_3$
DECOMPOSITION AT LOW TEMPERATURE ($480^\circ$C)
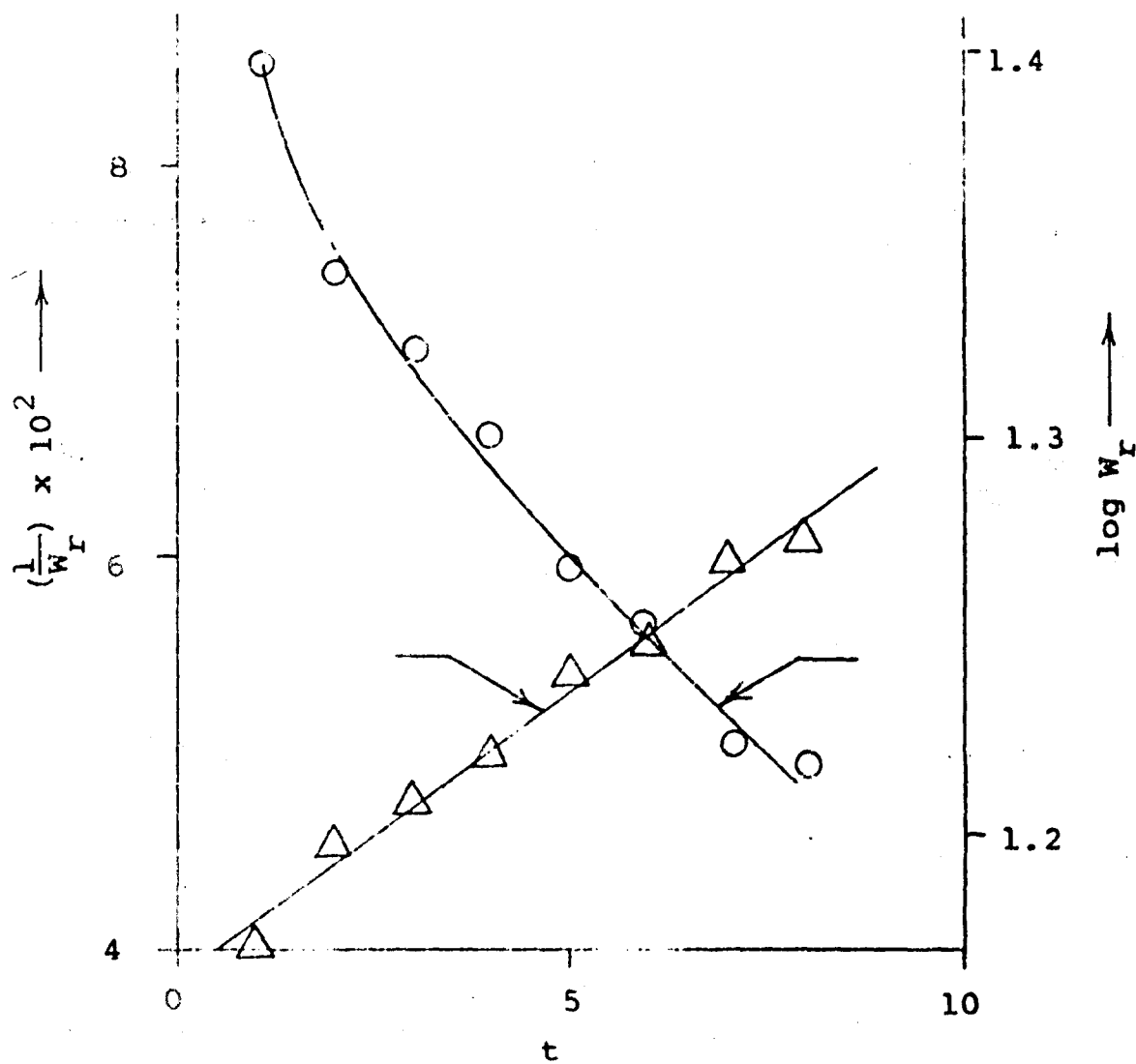
$() =$ 1st order plot

$\triangle =$ 2nd order plot

time factor:  1 unit $=$ 16 min

Figure 11

ORDER OF REACTION OF ISOTHERMAL DECOMPOSITION
OF POTASSIUM CHLORATE AT 450°C

Slope 2.28
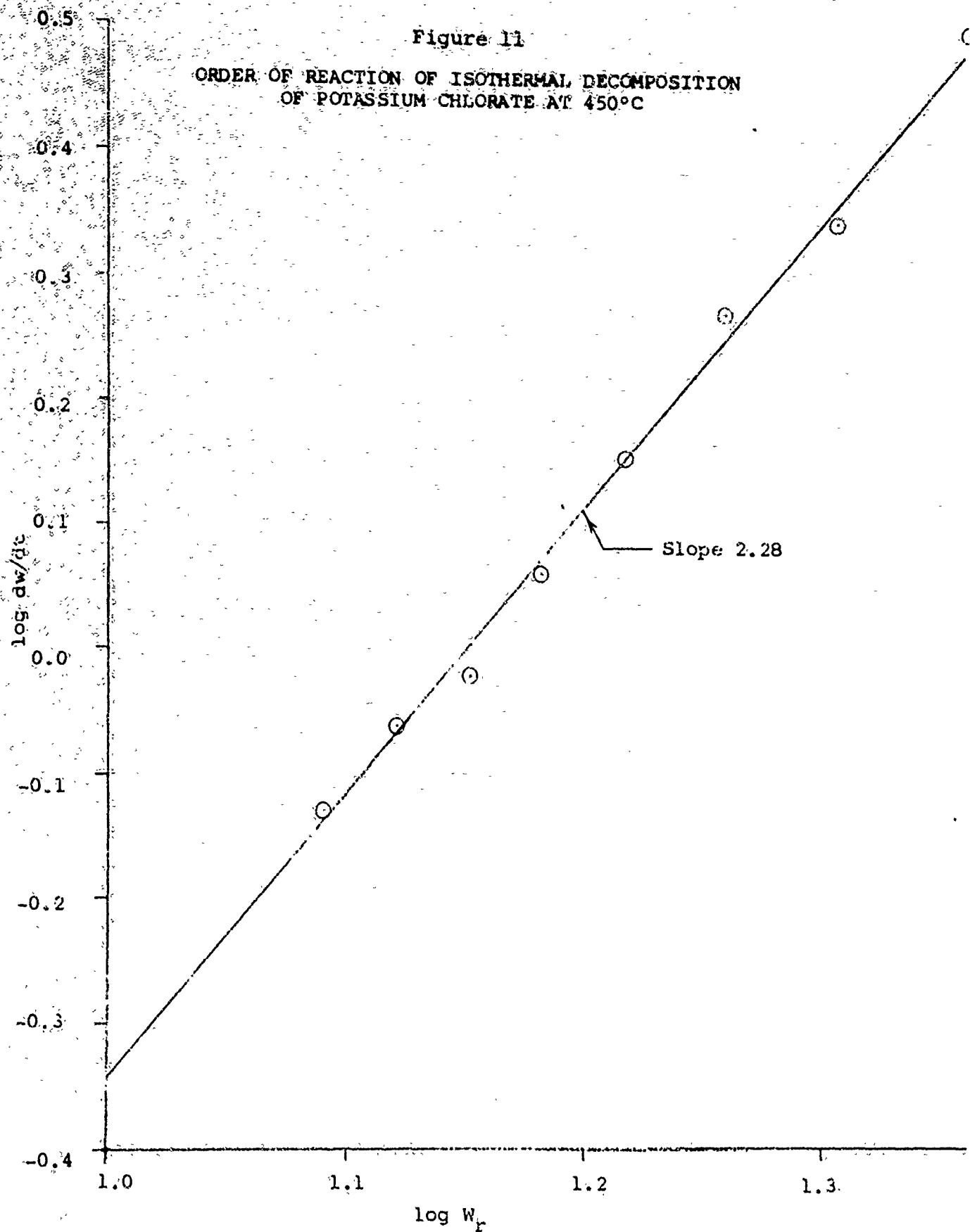
The hypothetical $ClO_2^-$ ion is very unstable at the temperature of reaction and decomposes spontaneously to $Cl$ and $O_2$.

$$[ClO_2]^- \rightarrow Cl^- + O_2 \qquad (2)$$

This is consistent with the finding that $KClO_2$ decomposes upon heating above $160°C$.[8] The above postulated mechanism is also in agreement with the observation that there is no appreciable change in thermal decomposition characteristics in an oxygen atmosphere, compared to that in an inert atmosphere. (See Figure 10 in Ref. 3).

The influence of KCl as a reaction product on the decomposition of $KClO_3$ was found to vary with concentration. TGA and DTGA experiments indicated that at high relative concentration (mole ratio 1:1) the KCl appears to retard the reaction at lower temperatures. (See Figure 19 of Ref. 3). Isothermal runs (Figure 2) at $480°C$ confirmed this.

At high temperatures and intermediate mole ratios of $KCl/KClO_3$ the KCl appears to accelerate the decomposition of $KClO_3$. (See Figure 42 of Ref. 3). One has to conclude that two opposing mechanisms govern the influence of KCl on the decomposition of $KClO_3$. At low temperatures and/or high concentrations of KCl, the KCl acts as a diluent, and the reaction is partially suppressed. At high temperatures and intermediate concentrations, the KCl additive acts as a catalyst. This catalytic action of KCl is born out by the observation[5] that KCl of different histories influences the decomposition of $KClO_3$ differently. It was found that reagent grade KCl has a

different apparent catalytic effect on $KClO_3$ decomposition than $KCl$ obtained originally from total decomposition of pure $KClO_3$. The maximum apparent catalytic effect is approximately at a mole-ratio of $KCl:KClO_3$ of 1:3 to 1:2. This might possibly be an indication that $KCl$ could activate a bimolecular $\begin{bmatrix} O & O \\ OCl\text{---}OCl \\ O & O \end{bmatrix}^{-2}$ anion to decompose more readily than in case of the pure decomposition. It is quite possible that polarization centers are formed by the additive which distort the electron distribution in the above anion.

It should be of theoretical interest, to compare quantum mechanically the $ClO_3^-$ ions with $ClO_4^-$ and $ClO_2^-$ and the above hypothetical bimolecular transition state. A priori calculations of the energy differences could yield an activation energy comparable to the actual value. The intermediately formed $KClO_4$ decomposes further via two apparent paths (See Figure 35, Ref. 1):

First

$$KClO_4 \rightarrow KClO_3 + 1/2 \ O_2$$
$$KClO_3 \rightarrow KCl + 3/2 \ O_2$$

Second

$$KClO_4 \rightarrow KCl + 2 \ O_2$$
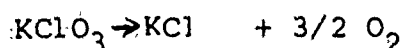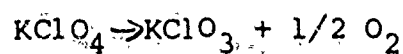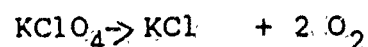
The intermediately reformed ($KClO_3$) is rather unstable at these higher temperatures and decomposes almost instantaneously to $KCl + O_2$.

Some authors claim[5] that $KClO_4$ also catalyzes the decomposition of $KClO_3$. To verify this, TGA and DTA runs were performed

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on various mixtures of $KClO_3$ with $KClO_4$. The weights were
approximately adjusted in such a way that the total weight loss
was approximately the same in all cases. It is seen from Figure 1
that in no case is an acceleratory effect on the decomposition
of $KClO_3$ observed. This and the catalytic action of dopants
described below leads us to believe that the above mentioned
authors had worked with impure materials which could possibly
have acceleratory effects on the decomposition of $KClO_3$.

## B. Decomposition of Doped, Irradiation, and Mechanically Shocked $KClO_3$

The decomposition of potassium chlorate is significantly
altered by small amounts of impurities. Figures 3 and 4 and
Table 4 show that, in particular, cations of transition elements
such as $Fe^{+++}$ and $Cu^{++}$ can lower the decomposition temperatures
by more than 200 C. In fact both, $Cu^{++}$ and $Fe^{+++}$ doped, samples
initiated decomposition in the solid phase before the melting
endotherm occurs. In Figure 12, the average decomposition
temperatures at 50% reaction are plotted as a function of
the charge density. The charge density is obtained by dividing
the cationic charge by the surface area of an assumed spherical
model of the impurity cations based on the published ionic radii.[9]
It appears that the decomposition temperature is decreased with
increasing charge density of the dopant cation. This may indi-
cate that the polarizing power of the doping cation on the
asymmetric electron distribution of the $ClO_3^-$ anion is an im-
portant factor in the reactivity of the doped potassium chlorate.

Figure 12

REACTIVITY OF DOPED $KClO_3$
(TEMPERATURE AT 50% DECOMPOSITION AS FUNCTION OF CHARGE
DENSITY AT SURFACE OF CATIONIC SPECIES)
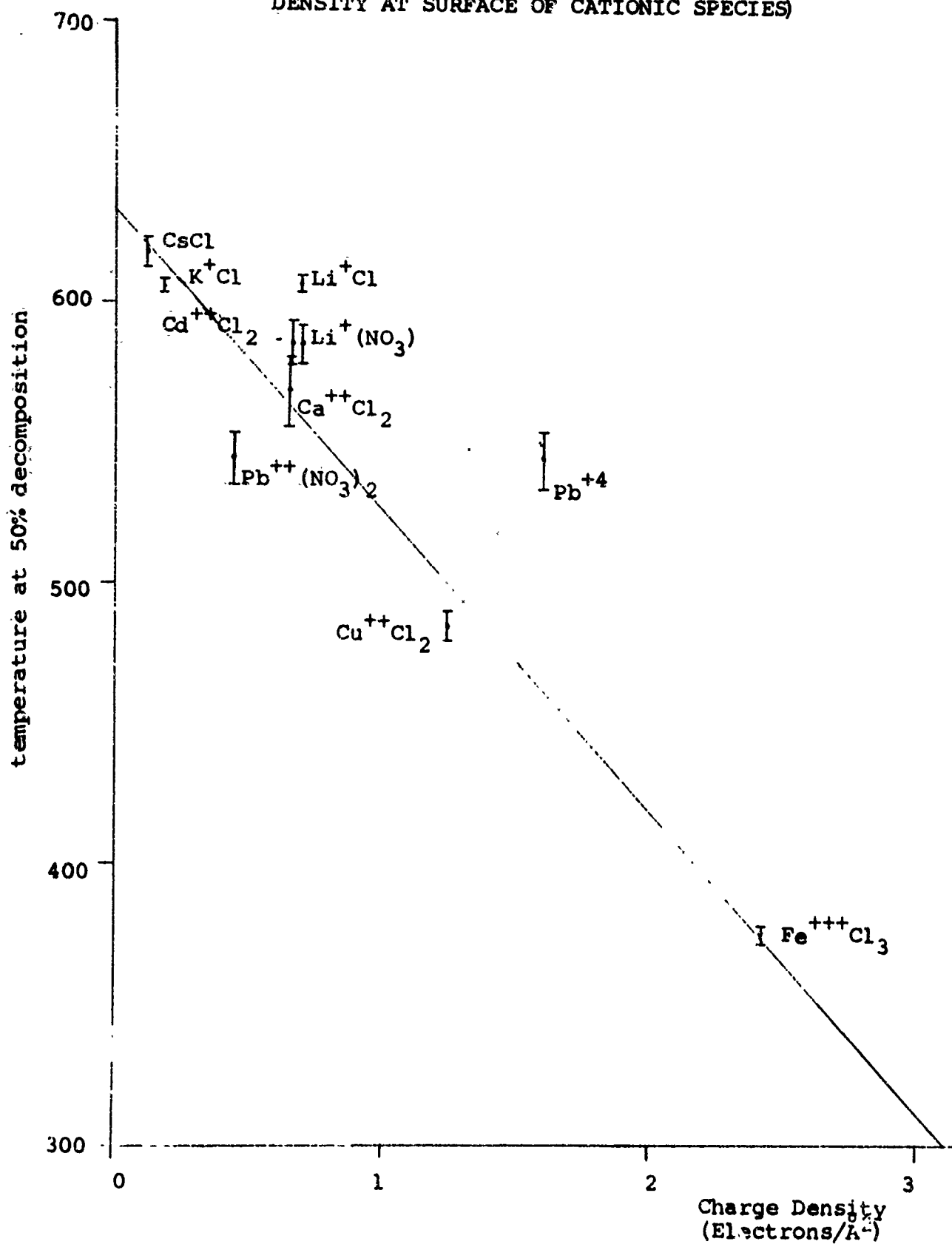
It should be kept in mind that the $KClO_3$ was in the molten state during this stage of these reactions. Doping with $CuCl_2$ caused appreciable increases in the chemical reactivity of $KClO_3$. In addition, it is also apparent that the first step of decomposition due to disproportionation is significantly more pronounced in the presence of these dopant cations.

In Figure 12 the reactivity of the lead dopant is plotted twice. In one case a doubly charged $Pb^{++}$ ion was assumed and in the other case a valence $+4$ was assumed, $Pb^{+4}$ ion. The point for the double valent $Pb^{+2}$ ion dopant lies left of the line, while that of the $+4$ valent $Pb^{+4}$ dopant lies to the right of the line. One interpretation may be that the lower valent lead dopant is partially oxidized to a higher valence state by the strong oxidant host compound.

The apparent catalytic effects may be considered from another point of view. This concept is based on the finding that the activation energy for thermal decomposition is about 50-55 kcal/mole. Based on this one would expect that if the rate controlling step in the thermal decomposition of $KClO_3$ involved the rupture of the Cl-O bond in the $ClO_3^-$ ion, then the marked effects of the $Fe^{+3}$ and $Cu^{+2}$ ions could not be accounted for. However, if the impurity cations could act as bridges in an electron transfer rate controlling mechanism then the marked reductions in decomposition temperatures may be reasonably expected. The reaction involves the formation of an intermediate $Fe^{+2}$ ion with a $ClO_3$ radical. The radical would

be considerably more reactive than the $ClO_3^-$ ion. The following equations illustrate this mechanism.

$$ClO_3^- + Fe^{+3} \rightarrow Fe^{+2} + ClO_3$$

$$ClO_3 + ClO_3^- \rightarrow Cl_2O_6^{-1}$$

$$Cl_2O_6^- \rightarrow 2\ Cl + 3\ O_2$$

$$Cl + Fe^{+2} \rightarrow Cl^- + Fe^{+3}$$
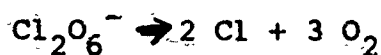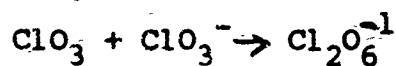
A similar mechanism would apply to $Cu^{+2}$ ion dopant. This mechanism can apply to the molten state or solid state decomposition. The activation energy for the interaction of 2 chlorate species would be reduced because of the formation of the intermediate chlorate radical. In the case of solid state decomposition, however, another factor such as defect state also becomes important which determines the concentration and mobility of charge carriers during charge transfer. The addition of higher valent cations may cause a reduction of positive holes or an increase of electrons in the conduction band. Another possibility is that the concentration of cationic vacancies would increase.

An estimate of order of activation energies of the doped potassium chlorates were made from the thermogravimetric curves obtained in the Chevenard DTA/TGA experiments. A method is described in the literature, where the inflection point in the TGA curve is determined.[10] The final equation is as follows:

$$\frac{E^*}{n} = -(RT_1^2/W_i)\ (dw/dt)_i$$

where $E^*$ is the activation energy, $T_i$ the temperature at the inflection point; $w_1$ the weight loss at the inflection point;

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n is the order. It should be noted that using this expression we are comparing $E^*/n$, rather than an activation energy alone. This however, does give information concerning the relative activation energies for comparison purposes.

Table 8 summarizes some of the values of $E^*/n$. It can be seen that there is wide scatter which is due to the qualitative nature of the Chavenard TGA runs. In particular, $(dw/dt)_i$ is rather difficult to determine.

From Table 8 we can, nevertheless, see certain trends in the activation energies:

The order of activation energies is in the order of dopants: None $>$ CsCl $\sim$ CaCl$_2$ $>$ LiCl $>$ Pb(NO$_3$)$_2$ $>$ CdCl$_2$.

The activation energy trends for the Cu$^{++}$ and Fe$^{++}$ doped samples were not evaluated, since the transition from solid state to molten state decomposition complicates the TGA-curves.

It is seen from the above equation that an order of two for the disproportionation mechanism, if applied to the doped chlorates would indeed double the apparent activation energies.

Irradiation with gamma rays seems to introduce a change in reactivity with respect to decomposition. The odor of chlorine and/or chlorine oxides indicates that irradiation creates radicals such as ClO$_3$ which decompose at much lower temperature than the ClO$_3^-$ anion. The radical formation does not

## Table 8

### APPARENT ACTIVATION ENERGIES OF DOPED $KClO_3$

| Dopant | $E^*/n$ Kcal/mole | Average Kcal/mole |
|---|---|---|
| None | 56.8 | |
| None | 62.3 | |
| None | 52.3 | |
| None | 52.5 | 56.7 |
| None | 50.4 | |
| None | 61.4 | |
| $CaCl_2$ | 50.7 | |
| $CaCl_2$ | 51.9 | 52.5 |
| $CaCl_2$ | 54.8 | |
| $CsCl$ | 46.4 | |
| $CsCl$ | 61.2 | 52.2 |
| $CsCl$ | 49.1 | |
| $LiCl$ | 40.4 | |
| $LiCl$ | 32.8 | 41.9 |
| $LiCl$ | 52.5 | |
| $Pb(NO_3)_2$ | 21.3 | 22.5 |
| $Pb(NO_3)_2$ | 24.5 | |
| $CdCl_2$ | 20.8 | |
| $CdCl_2$ | 17.1 | 17.7 |
| $CdCl_2$ | 15.1 | |

appear to be stoichiometric in view of the observation that sufficient $KClO_3$ is still left to create a large endotherm at around 360°C. This endotherm, however, shows shoulders indicating eutectics formed by the residual $KClO_3$ and some reaction product.

The nonstoichiometric nature of the low temperature release of gaseous products is also born out by the fact that one sample which underwent mechanical shock shows much less weight loss even though the DTA peak is approximately at the same temperature indicating a similar reaction.

The observation that the samples dried at room temperature in a desiccator, do not show the initial weight loss suggests that the reaction products are either very unstable and of low boiling point, or they are loosely sorbed within the irradiated defect crystalline structure and diffuse slowly to the surface, where they desorb under the force of concentration gradient set up by the drying agent in a desiccator.

### C. The Reaction Between Potassium Chlorate and Sulfur, $O_2$, Argon and Water

Preliminary DTA/TGA experiments were carried out with various mixtures of sulfur and doped potassium chlorates. The potassium chlorate samples were obtained from evaporation of 1% dopant in $KClO_3$ solutions. This was done to investigate the influence that doped $KClO_3$ has on the combustion of sulfur.

Table 5 summarizes the results in terms of combustion temperature. The average values of the combustion temperatures and the corresponding error limits (standard

deviations from these values) are comiled in Table 6.
The combustion temperature is lowest with $KClO_3$ doped with 1%
$CuCl_2$. The ignition temperature is reduced by more than 20°C
as compared to the ignition temperature of the undoped chlorate.
The effect of the dopants on the ignition temperature is $CuCl_2 \ll$
$KCl \sim Undoped \sim CsCl \sim Pb(NO_3)_2 < FeCl_3 \lesssim CdCl_2 < LiCl \sim LiNO_3 \sim CaCl_2$.
It is interesting to note that $FeCl_3$ is much less active as far
as the combustion temperature is concerned than $CuCl_2$. It should,
however, be pointed out that the average weight loss is much
higher with $FeCl_3$ than with all the other dopants. The
stoichiometric weight loss according to the equation:

$$2KClO_3 + 3S = 2KClO + 3SO_2$$
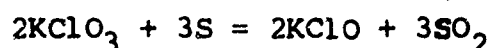
is approximately 37.6%. The actual weight losses are much higher.
This is a consequence of the vigorous reaction which forces
material out of the crucible. The fact that the average weight
loss in case of $FeCl_3$ as the dopant is much higher than with all
other dopants indicates a much faster reaction rate. Unfortunately,
the TGA curves show almost instantaneous weight losses so that
differences between reaction rates cannot be distinguished. To
overcome this difficulty, several trial experiments were run with
faster recorder speeds. Even with a recorder speed of 1 sec/inch
under dilute conditions, where additional $KClO_3$ acted as a diluent,
we were not able to detect significant differences in combustion
rates between doped and undoped $KClO_3$ mixtures. This indicates
that the rates are too fast and that the recorder is the limiting
factor.

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It had been observed that mixtures of sulfur with $Fe^{+++}$ and $Cu^{++}$ doped $KClO_3$ slowly released accumulated $SO_2$ gas which has a distinct odor.

Mass spectrometric analysis of a mixture of $KClO_3$-S heated in vacuum above 70°C showed a peak at mass 64 indicating the probable presence of $SO_2$ and/or $S_2$.

Preliminary conductivity measurements on a potassium chlorate pellet in air showed relatively high conductivity at low temperatures which were no longer present in vacuum (Figure 6). It was speculated that moisture in the air was the reason for this behavior. This was verified by experiments in dry atmospheres of air, argon and oxygen and the pellet did not exhibit the high conductivities at low temperatures. Rather, the curves appear to be similar as that in vacuum (Figure 8), and the activation energy calculated for the high temperature charge transfer was about 32 kcal/mole (Figure 7).

If the experiment was run, however, in water vapor, (Figure 8), the low temperature conductance was again observed. This might indicate that $H_2O$ molecules adsorbed on the pellet surface contribute considerably to ionic surface conductivity of perhaps solvated surface ions. This conductance disappeared as soon as the water was removed in vacuum.

Conductivity experiments in dry sulfur vapor did not yield conclusive results.

The influence of metal oxide additives on the combustion of mixtures of potassium chlorate and sulfur was probed by differential
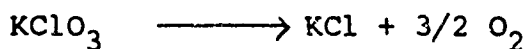
thermal analysis. The oxides considered were $Fe_2O_3$, $Cr_2O_3$ and $Al_2O_3$. These oxides were selected since the first two were found to be excellent catalysts while $Al_2O_3$ was relatively inactive. The concentration of the oxides were varied from 5 to 30 mole percent. These runs were generally performed in an argon atmosphere. A few experiments were carried out in an oxygen atmosphere. In an argon atmosphere the possibility of air oxidation is eliminated limiting the oxidation of sulfur to reaction with the $KClO_3$ in the mixture. Carrying out the reaction in pure oxygen emphasizes the role of air oxidation in the combustion reaction. Table 7 shows the results. It can be seen that the apparent ignition temperature differs significantly depending on the mole ratio of the metal oxide to potassium chlorate. It should be pointed out that there was a rather wide spread of experimental points, and, therefore, only general trends can be discussed. Additional experiments would undoubtedly result in data with improved precision. Because of the limited effort most of the work was confined to $Fe_2O_3$. If one considers the general trend of the results with the $Fe_2O_3$ additive, it appears that with increasing oxide content, to 5 mole % oxide, the principle effect is an increase in the ignition temperature. This would occur if the relative amount of oxide, or active oxide surface was less than optimum. As additional $Fe_2O_3$ oxide is added and the optimum ratio of catalytic activity is approached there is a minimum in the ignition temperature curve which represents the maximum lowering of the

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ignition temperature. This occurs at the mole ratio of
oxide to $KClO_3$ of 1/10. As the optimum amount of catalyst
is exceeded, the additional oxide probably acts as a diluent,
as evidenced by the increase in ignition temperature. Since
only one mole ratio was considered in the cases of aluminum
oxide and $Cr_2O_3$ additives, little interpretation can be
given to these results. It appears, however, that these
oxides are significantly less active than ferric oxide at
the 1/10 mole ratio. On the other hand it may be noted that
in oxygen the ignition temperature of the mixture containing
$Cr_2O_3$ was appreciably reduced, and was comparable to the
$Fe_2O_3$ containing compositions. There was also a slight
decrease in the ignition temperature of the mixture con-
taining $Fe_2O_3$ in the presence of oxygen. Possibly $Cr_2O_3$
and $Fe_2O_3$ can act as catalysts for the reaction between
sulfur and oxygen. At the mole ratio of 3/10 oxide of
$KClO_3$ it is seen that, with an increase in concentration of
sulfur from stoichiometric to double the stoichiometric
amount, the ignition temperature was reduced. In summary, the
most significant findings appear to be those for the compo-
sitions containing the $Fe_2O_3$ catalyst where a minimum in the
ignition temperature curve occurs at the mole ratio of
oxide to $KClO_3$ of 1/10. Further experiments, however, will
be required before definite conclusions can be reached.

## V. CONCLUSIONS

1. The results indicate that the decomposition of potassium chlorate occurs in the following steps:

$$2 \ KClO_3 \xrightarrow{\text{slow}} KClO_4 + (KClO_2) \text{ unstable (2nd order)}$$

$$(KClO_2) \xrightarrow{\text{instantaneously}} KCl + O_2$$

$$KClO_4 \longrightarrow KClO_3 + 1/2 \ O_2$$

$$KClO_3 \longrightarrow KCl + 3/2 \ O_2$$

$$KClO_4 \longrightarrow KCl + 2 \ O_2$$
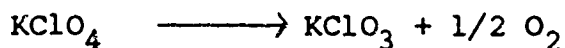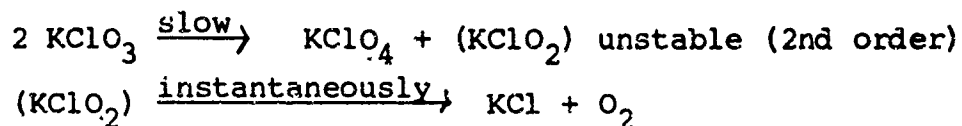
The first disproportionation reaction is consistent with a second order mechanism and is inhibited at low temperatures by excessive amounts of KCl. At high temperatures, KCl catalyzes the reaction.

$KClO_4$ does not catalyze decomposition of $KClO_3$. At higher concentrations, the decomposition of $KClO_3$ is inhibited in the presence of $KClO_4$.

2. The order of dopants with respect to decreasing the decomposition temperatures of doped $KClO_3$ was found to be: the most effective, $FeCl_3 > CuCl_2 > Pb(NO_3)_2 > CdCl_2 > CaCl_2 > LiNO_3 > LiCl > KCl \sim CsCl \sim$ No Dopant. This order can be correlated to charge density or to charge transfer. Doping $KClO_3$ with nitrates reduces the temperature of the DTA endotherm for melting.

3. Gamma irradiation and mechanical shock influences the decomposition path of $KClO_3$. Low temperature weight loss and smell of chlorine and/or chlorine oxides point to defect creation of possible radicals such as $ClO_3$ within the crystalline lattice due to irradiation. An exotherm appears at about 75°C in the DTA curve for the mechanically shocked sample which does not appear in the untreated sample.

4.   Doping of $KClO_3$ significantly influences the ignition of mixtures of $KClO_3$ and sulfur.  Two effects are apparent: The order of ignition temperatures with reference to the dopants is:   lowest for $CuCl_2 \lesssim KCl \sim$ undoped $\sim CsCl \sim Pb(NO_3)_2 < FeCl_3 \lesssim CdCl_2 < LiCl \sim LiNO_3 \sim CaCl_2$.

The extent of total weight loss as measured in the TGA experiment is dependent on the rate of combustion since the rapid ignition forces material out of the reaction vessel. This is particularly true for the $FeCl_3$ doped samples.  $Fe^{+++}$ and $Cu^{++}$ doped $KClO_3$ appears to react slowly at room temperatures with sulfur.

5.   The reactivity of sulfur-$KClO_3$ mixtures is especially affected by the presence of $Fe_2O_3$ catalyst.

In oxygen the ignition temperature of the sulfur-potassium chlorate mixture is significantly lowered in the presence of the $Cr_2O_3$ and $Fe_2O_3$ catalysts.

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**13. ABSTRACT**

The effects of defect structure and doping of potassium chlorate on its chemical reactivity with respect to its propagative reactions with sulfur was investigated.

The preparation of doped single crystals of potassium chlorate was continued during the entire program. The crops of single crystals were analyzed for their dopant contents. The influence of doping on the thermal decomposition of potassium chlorate was investigated by DTA and TGA.

The effect of potassium chloride and perchlorate as an intermediate reaction product on the thermal decomposition of potassium chlorate was studied. These experiments are necessary for establishing the basis for evaluating the reactivity of potassium chlorate with sulfur.

Electrical conductivity studies were initiated to correlate electronic defect structure with the reactivity behavior of potassium chlorate. Low temperature isothermal investigations were conducted to evaluate possible reaction mechanisms.

The effect of irradiation and mechanical shock on the decomposition of potassium chlorate was probed.

The combustion reaction of mixtures of sulfur with doped potassium chlorate and of mixtures with selected metal oxides was investigated.

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Activation energy
Cadmium chloride
Calcium chloride
Cesium chloride
Combustion temperature
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Differential thermal analysis
Doping
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Electronic defect structure
Gamma irradiation
Iron (III) chloride
Lead nitrate
Mechanical shock
Potassium chlorate
Potassium chloride
Potassium perchlorate
Single crystals
Sulfur
Thermogravimetric analysis

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# SUPPLEMENTARY

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